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Canadian Centre for Mineral and Energy Technology (CANMET)

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CANMET

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TITLE **REF. NO.: 12**

Abrasion Resistant Glass-Ceramic Tiles for Materials Handling Systems.

DESCRIPTION

Compositions have been developed that are suited to the production of abrasion resistant tiles formed by recrystallization from a melt. The abrasion resistant phases are principally alkaline silicates and may readily be produced from modified steel slags. These materials are more resistant to abrasion than steel, but less than alumina.

APPLICATION

These tiles can be used as liners for chutes and bins under abrasive and corrosive conditions in materials handling systems, found in mining, milling and other industries.

ADVANTAGES

Abrasive resistant lining plates are expected to reduce substantially metal wear costs which range from $10 to 100 million per year as estimated for the Canadian mining and related industries.

DEGREE OF DEVELOPMENT

Determination of the correct compositions has now been completed at the laboratory stage, including appropriate nucleating additives and recrystallization temperatures. Abrasion tests have been carried out. The forming technology has yet to be developed in North America.

LICENCE

Patent application is being considered. Acquisition of know-how can be negotiated.

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1.0 Introduction

Research has been conducted by the Ontario Research Foundation and the Canada Centre for Mineral and Energy Technology for developing an abrasion-resistant glass-ceramic tile for use in material handling systems with slag as a principal component. This report examines the marketing implications for this product including competition, applications, success factors and market structure. As well, work done in other countries on slag-ceramics and the research completed in Canada is summarized.

The work presented in this report has been conducted under the auspices of the Small Business Consulting Service of McMaster University in Hamilton.

2.0 Slag and Its Utilization

From the Iron Age, and right up to the beginning of the present century, slag was a waste product of pyrometallurgical operations. Blast furnaces often produce one tonne of slag for each tonne of metal. The interest of early ironmasters was restricted to the cheapest and quickest way of disposing of it. This often led to huge slag hills which blighted the landscape around great smelting works.

To get a feeling for the immensity of the slag problem, the annual production of blast furnace slag in the leading iron-producing countries of the world in 1967 was as follows:

Table 1

World Slag Production (Ref. 1)

Country	million tonnes
U.S.A	30
Germany	15
Japan	15
France	13
U.K.	11
Russia	9
Canada	7

Of course, since 1967 less slag has been produced and the trend to higher grade ore has, perhaps, reduced the production of slag.

In Canada, as in Britain, slag has been primarily used in the construction of roads as road bases and surfaces. There are other uses for slag and these are presented in Table 2. The pre-eminent treatment of slag is to crush it and use it as a building agent. However, the purpose of this report is to examine the economic potential of the final listed use-- slag ceramics.

Table 2

Uses of Slag (Ref. 1)

Road Bases
Road Surfacing
Railway Track Ballast
Concrete Aggregate
Filter Media
Granulated Slag in Cement Manufacture
Slag Wool for Heat Insulation
Slag Ceramics

2.1 Slag Ceramics: A Description

The simplest definition of a "slag ceramic" would be a chemically modified blast furnace slag into which nucleating agents have been added. The remelted product is cast in moulds to give the required shape and then heat treated to produce controlled fine crystalline structures.

Among the desirable properties slag ceramics possess are: 1) excellent abrasion-resistance; 2) scratch hardness of between 7 and 9 on the Mohs scale; 3) good resistance to weather and chemicals; and 4) a high crushing strength. To the negative, it appears that slag ceramics are susceptible to thermal shock.

Though work on slag ceramics dates from the early 1960's, it appears that to date North America has done little to develop the technology here.

3.0 History of Slag Ceramics

This section attempts to summarize the advances in and experiences with slag ceramics. From the literature, it would appear that slag ceramic work has been confined to the Soviet Bloc nations, Great Britain and Japan.

3.1 The Russian Experience (Ref. 2, 3, 4, 5)

The use of blast furnace and electro-furnace slag in the manufacture of ceramic tiles dates to the early 1960's. Originally developed to meet a government-inspired recycling plan, the "slag-sitall" tiles were found to have very desirable anti-abrasive and corrosion-resistant properties. As the alumina that is used in traditional abrasion-resistant tiles was in short supply, the "slag-sitall" experiment was developed into a pilot plant operation.

If the Russian journal articles are a measure of progress, then the field of slag ceramics in the Soviet Bloc nations has really mushroomed. One such advance has been in coloured tile. Though the original "sitall" tile had a brownish-gray colour, tiles are now being produced that are bright red, blue, green, gray, dark gray and white. The latter has been produced using sodium sulfate waste.

The uses for these tiles in the Soviet economy include: inside and outside facing of walls, industrial and home floor coverings, electrical insulators, pipe, sanitary ware and as abrasion and corrosion-resistant protection for equipment in the mining and chemical industries. The reported cost of slag sitalls ~~are~~ is about \$39-\$67/tonne of sheet but these figures are 15 years old. It is worth noting that in several of the journal articles savings and profit figures are quoted ranging from 67,000 to 1.5 million rubles (100,000 to 2.7 million Canadian \$). While these savings are noteworthy, it is difficult to say if they are attainable in Canada, as the similarities between the Russian and Canadian economies are few!!

3.2 The British Experience (Ref. 6, 7, 8)

[illegible] process. Mayhew mention. Did not want to produce patent.

Through the efforts of the British Iron and Steel Research Association (BISRA), the Russian technology spread to Britain and in 1960 British scientists introduced "slag ceram". Work progressed through a small pilot plant accommodating 20 pound samples to a larger plant accommodating 200 pound samples that was in part financed by United Steel Co. and C.B.P. Engineering and Construction Limited. At the larger scale several technical problems were discovered. These included difficulties in achieving uniform temperature conditions in the melt, rapid changes in melt viscosity with temperature and problems in the "gobbing" stage. As the resulting product was to be used heavily in the mining industry, the downturn in the economy, which so greatly affected mining in the late 1970's, caused the project to be abandoned.

While the project was underway, the "slag ceram" was marketed under the trade name Basramite. Colours were available and these included black, grey, white, orange, brown, red-brown and green. As well a colourless tile was available. In industrial situations, it was used as a replacement for basalt in abrasive environments. Specific applications included: an abrasion-resistant chute lining for handling iron ore and coke, a tile floor in a busy office and office passage, an industrial floor exposed to heavy equipment and a floor covering for use around a small furnace (at floor temperatures of 90° C). Other applications that were envisaged include: stair treads, fence posts, lintels, tunnel lining, sea defenses (breakwaters), dams, non-skid road surfaces, paving flags, kerbstones, guttering and drain pipes. These were never tested.

For the British, the product never became economical. The major cost was the energy required for the heat treating of the tile. Further a plant needed to be producing at least 300 tons of "slag ceram" per day for the process to be economical and it was felt that the demand for wear-resistant tiling would never reach that point.

3.3 The Japanese Experience

Little has been published relating to the Japanese slag ceramic industry. NGK Insulators Ltd. of Japan applied for a patent on February 23, 1965 (U.S. Pat. 3,170,780) but it is not known if it was granted. In examining the product, the British claim that it had similar properties of abrasion-resistance and hardness but it seemed that the bending strength was higher than for the British and Russian products.

[illegible] of slag [illegible] in Britain [illegible]

NGK spark plug holder

4.0 Slag Ceramics in Canada

This section reviews the work done to date by the Ontario Research Foundation (ORF) in developing "slag ceramic" technology in Canada. This review is presented from a non-engineering viewpoint and serves to highlight the history of the product to date.

4.1 Phase One (Ref. 9)

Though "slag ceramics" were announced to the world in the 1960's, the work in Canada began in 1980 when the Canada Centre for Mineral and Energy Technology (CANMET) commissioned research in the field of abrasion-resistant ceramics and glass-ceramics. This early work showed that the production of such materials was possible and that these materials had improved abrasion-resistance. The source of the improvement and the effects of heat treatment on the melt were questions unanswered at this stage. Also noteworthy was the development of a new technique to determine the abrasion-resistance of ceramic and glass samples. At this stage, though, slag was not mentioned as a possible material.

4.2 Phase Two (Ref. 10)

The results of the 1980 work were encouraging enough to launch a follow-up study in 1982. This time glass ceramics were produced from compositions of alumino-silicate, basalt and slag. Again, the purpose of the research was twofold: 1) to develop materials with improved abrasion-resistance; and 2) to study the effect of heat treatment on hardness and abrasion-resistance. Fifteen different mixtures were prepared and tested. All had desirable abrasion-resistance properties and the glass-ceramics based on basalt and slag possessed high mechanical strength. As for heat treatment, it was found that the temperature maintained throughout the nucleation time and the time allotted for nucleation were key factors affecting the abrasion-resistance of the material.

In this research, glass number 15 was produced from blast furnace slag whose origin was a Hamilton steel plant. This glass was composed of 56% slag, 28% sand, 4.8% sodium carbonate, 5.6% sodium sulphate, 4.5% silica and 1.19% alumina. This research still left unanswered the questions of optimum composition and optimum heat treatment.

4.3 Phase Three (Ref. 11)

As slag is a large and somewhat unutilized waste product of metallurgical operations in Ontario and as slag is a rather inexpensive and readily available material, a third study was completed in 1983. This study looked at the effects of nucleating agents and heat treatment on slag-ceramic mechanical strength and abrasion-resistance.

At this stage the production process went as follows: 1) ball milling of raw materials for two hours; 2) calcination of raw materials at 600° C for approximately 8 hours; 3) melting was done at 1440° C and the material was allowed to soak for up to 5 hours; 4) nucleation occurred at 720° C for 10 hours; and 5) crystallization took place at 900° C for 3 hours. (This is a non-engineer's interpretation of the work.) Though the raw materials may be cheap, this procedure requires a large amount of heat and is likely a key cost factor.

On average, the glass ceramics contained 72% slag, 22% sand and the remainder nucleating agents (either TiO_2 and Cr_2O_3 or Fe_2O_3 and carbon). In the study the glass ceramics consistently outperformed the glasses. As well, the Fe_2O_3 nucleating agent seemed to produce better abrasion-resistant material. Finally the moderate heat treatment or soaking of 3 hours seemed to produce better abrasion-resistance.

As before this research has left some questions unanswered: 1) What is the relationship between the nucleating agent (Fe^{++}/Fe^{+++}); 2) Can the heat treatment cycle be reduced to make the process more energy efficient? and 3) Can the strength and abrasion-resistance be improved through modification of the heat treatment procedure and perhaps by adding some alumina?

4.4 What Product Do We Have?

From the review of the research, it is obvious that what we are dealing with is more a product concept than an actual product itself. Though research is moving towards the creation of a finished product, the optimum raw material blend, the optimum procedure for melting, soaking, nucleating and crystallizing are still unknown. Table 3 compares the Canadian, British and ~~American~~ Russian products.

Abrasion Resistance

Alumina > Slag ≃ Basalt

Table 3

Comparison of Slag Ceramics (Ref. 6, 11)

	Canada	U.K.	U.S.S.R.
Hardness (Mohs)	7.0-8.0	8.0-9.0	8.0-8.5
Coefficient of Thermal Expansion ($x10^{-6}$)	8.25	5.0	7.2
Abrasion Resistance	Twice Quartzite	Twice Basalt	N/A
Modulus of Rupture (PSI)	8,000	20,000	20,000
Density (gm/cm^3)	N/A	3.00	2.706
Chemical Stability in Conc. H_2SO4	N/A	Lightening in Colour	99.70%
35% NaoH	N/A	Brown Patches and all surfaces lighter	83.46%

This comparison confirms the last research done by ORF. For the material to be viable in the abrasion-resistant marketplace, it must become harder, stronger and more abrasion-resistant. Thus, there are truly two steps required before commercialization is feasible: 1) Development of improved slag ceramic with optimum composition, optimum heat application and optimum properties; and 2) If the optima can be found, development of small pilot plant operation to expand and refine the laboratory process and to help determine costings.

This finding will become more evident as the tile market is examined in the next section.

5.0 The Market for Slag-Ceramics

Looking at the work done in other countries the possible uses for slag ceramic tile fall into three categories: 1) Abrasion-Resistant Ceramic Tile; 2) Industrial Floor and Wall Tile; and 3) Tile for use in the home. Remembering that other countries of the world operate in a different economic climate (particularly the Soviet Bloc nations), the focus of this section is on Abrasion-Resistant Ceramic Tiles.

5.1 The Market for Abrasion-Resistant Ceramic Tiles (Manufacturers & Wholesalers) (Ref. 12 & 13)

At present, no one in Canada manufactures Abrasion-Resistant Ceramic Tiles. Consequently, anyone adapting the technology for use in Canada would have an abundant and cheap ($5/ton) raw material supply and a monopoly on the production of such tiles.

The reason why no one makes these tiles in Canada is unclear. Annual sales of A.R.C. tiles are on the order of $4-6 million. This demand is met by a series of wholesalers, the largest of which is Williams & Wilson Ltd. with five offices across Canada. They fill approximately 60% of the Canadian demand, while a second wholesaler, Thermalloy Corp., fills another 25% of demand. The remaining 15% is accommodated through contracting firms who provide a small amount of the tile as part of a larger job.

Most of the A.R.C. tile used in Canada is imported from the United States where annual sales of these tiles average $50-60 million dollars. * There are few manufactueres and the top five account for 95% of the sales. The largest producer is Coors Porcelain Co. located in Colorado. This firm produces about 40% of all A.R.C. tiles in America. By production size, the other four companies are: Champion Sparkplug (Michigan), Ferro Corp. (Ohio), Carborundum Co. (now known as PACKO, Pennsylvania), and Dimonite (Ohio). There are also European companies which produce A.R.C. tiles and the largest of these is Greenbank Terotech Ltd. of England.

employees have bought the plant

None of the U.S. mfrers. use slag, only alumina

5.2 The Market for Abrasion-Resistant Ceramic Tiles (Competitive Products) (Ref. 12, 13)

In the Abrasion-Resistant materials market, there are different competing products. About 10% of the business does not go to tiles at all but rather to rubber and rubberized linings. The remaining business is divided between three types of A.R.C. tiles: Cast Basalt, Alumina Oxide Tiles and Silicon Carbide Castings.

Cheapest

3x Basalt

Cast Basalt is made from the volcanic rock which is then melted and cast in to tiles. It is the cheapest type of tile and is approximately one-third the cost of alumina tiles. The major drawback of cast basalt is the thickness of the tiles-- 1-1/4" thick. Though the technology is improving and tiles may soon be produced that are 3/4" thick, the thickness makes them impractical for many applications. Thus they account for little more than 25% of the abrasion-resistant materials market in Canada (though they are used extensively in the European market).

Not good for curved surfaces

Alumina Oxide Tiles are the major player in this market accounting for 50% of the abrasion-resistant materials market. These tiles are usually white or grey in colour and come in a wide range of sizes and thicknesses. Table 4 gives a sampling of the sizes and widths available while Table 5 gives some of the tile costs.

Table 4

Alumina Oxide Tile Sizes and Thicknesses Available (Ref. 13)

Thickness	Size
1/8"	4" x 1", 4" x 2", 4" x 4", 6" x 4"
1/4"	4" x 1", 4" x 2", 4" x 4", 6" x 4", 6" x 2"
1/2"	6" x 2", 6" x 4", 4" x 3"
1"	6" x 4"
2"	6" x 4"

Table 5

Costs of Various Sizes of Alumina Oxide Tiles (Ref. 12, 13)

Size	Cost (Can. $, F.O.B.)	
6" x ~~4"~~ 2" x 1/4"	~~$1.56~~ $1.36	
6" x ~~2"~~ 4" x 1/4"	$1.62	
6" x 4" x 1/2"	$2.32	
4" x 3" x 1/2"	$1.56	
6" x 4" x 1"	$7.00	(Basalt ~ $2.00)
6" x 4" x 2"	$13.00	

Alumina Oxide Tiles also come in two varieties: plain and weldable. The tiles are attached either by epoxy resins or by welding. The only drawback to these tiles is covering oddly shaped or very small items.

For the latter items, silicon carbide is often used. Though the cost is more than alumina oxide, comparisons are difficult to make as silicon carbide is rarely cast into tiles. Instead it is cast into small pipes and odd-shaped pieces. Most of the work is done to custom-made specifications and is subject to their constraints. As it is more expensive than alumina-oxide tiles, it is never considered as a substitute but more as a complementary material. The remaining 15% of the abrasion-resistant materials falls into this category.

There are divisions below this level. There are different purities of alumina-oxide and different blends of cast basalt and silicon carbide. The discussion is meant to give one a flavour of the abrasion-resistant materials market. It should be noted that all A.R.C. tile on the market today suffer from an inability to withstand thermal shock. That is, in environments where there will be much heating and cooling, the tiles are susceptible to cracking and splintering.

5.3 The Market for Abrasion-Resistant Ceramic Tile (Applications) (Ref. 13)

The users of abrasion-resistant materials are quite varied. The two largest users are mines/smelters and power plants. In both cases these materials are used as liners for chutes, hoppers, silos, bins and raw material transport cars to protect metal surfaces from abrasion. In power plants, abrasion is from coal as opposed to ore. Interestingly, in areas where coal has been reduced to a fine dust, bathroom tiles are used in place of A.R.C. tiles to protect metal surfaces. Currently power plants in Ontario, Quebec, Alberta, Saskatchewan, Nova Scotia and New Brunswick use A.R.C. tiles in their operations. The average contract size from Hydro plants is $100,000-250,000.

Tiles contribute ~50% of this. Rest supplies + labour.

There are other smaller users. Some of them have similar abrasion-resistant needs. These include grain-handling facilities and heavy traffic shop floors. Laboratories make use of the chemical resistant properties of the tiles. For this application they are used for spark-resistant floors and in making crucibles and boats. Though it cannot be confirmed, Coors Porcelain is apparently working with the Israeli Military on a project using the impact resistance quality of A.R.C. tiles. One unconfirmed report even suggested A.R.C. tiles could be used in bullet-proof vests.

Zirconia reinforced alumina to increase impact resistance.

Though there are other users, mines/smelters and power plants are most likely to predominate the market for A.R.C. tiles. The purchases made by mines/smelters are often in the "retro-fit" area and the number of these is tied to the health of the industry. In the early 1980's, few companies were buying A.R.C. tiles but as the fortunes of mines/smelters have improved so have the sales. Power plant purchases are relatively stable and are part of a continuing effort to reduce costs and conserve resources. There is some concern that this market could become smaller in the future once all power plants have adopted A.R.C. tiles for use in their systems but this shrinkage is not likely to occur for some decades.

5.4 Key Questions Asked Within the Tile Market — by suppliers mfrs.

1. How does the material compare on abrasion resistance?
2. How does the material compare on price?
3. Is it thermal shock resistant?
4. What are the companies' capabilities to deliver, service and process the product?
5. What are the sizes and forms of the product?

5.5 Other Markets for Slag Ceramics (Ref. 14)

Slag ceramics possess a distinct advantage in their abrasion and chemical resistance. If one wants to use the material for industrial or home tiles, the need for chemical and abrasion resistance is greatly diminished and thus a competitive edge is lost.

For industrial floor and wall tile, the major consideration is cost. Companies are looking for a floor covering that is easy to care for and cheap to install. Patterns are definitely not a prime consideration but colour does play a role. The major product in this field is quarry tile and it sells for approximately 25% the price of A.R.C. tiles (Alumina). Certainly slag ceramic tiles can be (and have been) used for industrial floors but they must be produced at a low cost. To accomplish this, abrasion and chemical resistance could be reduced as the focus shifts to cost factors.

The tile market for home use is much more sensitive to colour, patterns and finish. Slag ceramics have been produced in a wide range of colours, but no patterns have ever been attempted. Because of their abrasion resistance, slag ceramics are very difficult to polish and come in an unfinished state. Consumers are also price-sensitive. A.R.C. tiles are about eight times the price of conventional home tile. The previous three problems are most likely eliminate the current O.R.F. slag ceramics from the home market.

6.0 The Next Step

From CANMET's perspective, the product is at a three-pronged fork in the road. Should the technology and the product be: 1) allowed to lapse?; 2) sold for commercialization?; or 3) developed further? Given the investment CANMET has already made in trying to develop the technology and the product, the first alternative would only be taken if there was no future for slag ceramics in Canada. At this stage in development, slag ceramics seem to have many economic and social advantages attached to them and so the first alternative will be dismissed.

To accomplish the second alternative more would have to be known about the technology and the product. Costing of the process, optimal blends of raw materials, optimal heating processes and comparative abrasion and chemical resistance tests would have to be done. These are not available at this time and it is unlikely a company would wish to buy an unproven and untried technology. The second alternative is thus dismissed. However, if someone did wish to purchase the technology at this point, CANMET might wish to seriously consider the offer!

The most likely course of action is further development of the product. This would most likely follow two stages. Phase one would include research into optimal mixes of materials and heating times. Hopefully sample ceramic tiles could be produced for testing. If these proved to be as abrasion-resistant as the material on the market, a second stage would be undertaken. Phase two would be the construction of a small pilot plant operation probably with a commercial partner. This would serve to test the technology in less of a research setting and could facilitate accurate costing. Costs of such a plant are unknown though there would no doubt be some government funding involved. At this stage the commercial partner might wish to buy the technology and expand the operation. Failing this, the technology could be offered to other companies both nationally and internationally.

There are good reasons to develop the technology further: 1) A company producing abrasion-resistant ceramic tile in Canada would be in a monopoly situation; 2) The rather inexpensive and abundant raw material could give the company a cost advantage in the market; 3) The social benefits of helping to clean the environment could be an advantage for gaining government grants and contracts for government businesses (power plants); and 4) Much of the groundwork development has been completed so the remaining R & D expenditures are considerably less.

The only danger in carrying the research work forward is that it may not be possible to develop an equivalent abrasion-resistant material from slag ceramics and/or the cost of producing the material would put it at a competitive disadvantage in the marketplace.

7.0 References

1. Lee, A.R. Blast Furnace and Steel Slag, John Wiley & Sons Ltd., New York, 1974.

2. Kislitsyn, B.F., Cholovski, M.F., Sas, R.I., Lynnik, L.I., Kurchagina, Z.F., and Yakovlev, A.V. "Using Electro Furnace Slag for Making Slag-Ceramic", Glass and Ceramics, March, 1982, pp. 116-17.

3. Kislitsyn, B.F., Sas, R.I., Kurchagina, Z.F., and Lynnik, L.I., "Sodium Sulfate Waste for Making Slag-Sitall Tiles", Glass and Ceramics, July, 1981, pp. 319-320.

4. Chernyak, L.P., Trubachev, V.I., and Pyshnoi, U.S. "Using Blast-Furnace Slag in Ceramic Melts", Glass and Ceramics, October, 1981, pp. 525-527.

5. Bazayants, G.V., Svetlichnyi, V.A., Denchuk, V.V., and Ryzlikov, V.A. "Abrasive Wear of Glass Enamels and Slag Sitall Used in Heat Energetics", Glass and Ceramics, June, 1983, pp. 265-296.

6. Klementaski, S., and Kerrison, B. "Slag Ceram, A New Construction Material", Chemistry and Industry, October 15, 1966., pp. 1745-1753.

7. Kirk-Othmer, Encyclopedia of Chemical Technology, "Slag Ceram", John Wiley & Sons Ltd., London, 1971., pp. 876-889.

8. Correspondence to Mr. Bob Cotsworth, National Slag Ltd., from George H. Thomas, British Steel Corporation.

9. ORF Report, "Development of Abrasion Resistant Ceramics", Dec. 31, 1980.

10. ORF Report, "Development of Abrasion Resistant Glass-Ceramics", April 30, 1982.

11. ORF Report, "Development of Abrasion Resistant Glass-Ceramics from Industrial Waste Products", May 26, 1983.

12. Conversations with Mr. Jim Hamlen, Thermallov Corporation, Richmond Hill, Ontario.

13. Conversations with Mr. Paul Verhev, Williams & Wilson Ltd., Toronto, Ontario.

14. Conversations with Mr. Mason, Hamilton Porcelains Ltd., Brantford, Ontario.

Appendices

Appendix A

Reference 1

4

The uses of slag

Slag is used as an aggregate for a wide variety of purposes. In Great Britain, by far the bulk is used for the construction and maintenance of roads. Abroad it is used widely as an aggregate for concrete, both for high-strength normal concrete and for lightweight concrete. It makes good quality railway ballast, and is one of the best aggregates for filter media in sewage purification plants.

It is the basis of Portland blastfurnace cement, and is used in vast quantities abroad for this purpose.

It is drawn into fibres for the manufacture of slag wool for heat insulation purposes.

The annual production of blastfurnace slag in the leading iron producing countries of the world in 1967 was as follows:

	million tonnes
U.S.A.	30
Germany	15
Japan	15
France	13
U.K.	11

It is probable that the world consumption is of the order of 100 million tonnes per annum.

Slag production in Great Britain had a peak value in 1967 of 11.7 million tonnes. It has fallen continuously since then to nine million tonnes in 1972. The amount of slag produced is dependent upon the amount of iron produced and upon the type of ore used. The trend to replace home-ore, containing only 20 per cent iron, by imported rich ore containing at least 60 per cent iron is a major factor in reducing slag production (see page 19).

Table 4.1 gives the quantities of slag used for various purposes in Great Britain for the year ending December 1972.

Table 4.1 Slag used in Great Britain during the year 1972

		thousand tonnes
A. Blastfurnace Slag (total) comprising:		7132
1. Air-cooled: used for		
(a) Roadstone, chippings, coated and uncoated macadam and asphalt	4991*	
(b) Rail ballast	238	
(c) Filter media	142	
(d) Concrete aggregate	264	
(e) Unrecorded uses	1296	
2. Foamed	183	
3. Granulated	18	
B. Steel Slag (total)		354

* About half is used for coated macadam and asphalt.

4.1 The construction and maintenance of roads.

4.1.1 SLAG IN ROADBASES

Great Britain—air-cooled slag

Slag has been used successfully for many years in road bases, either in the form of wet-mix or dry macadam, as tar or bitumen macadam, and as lean concrete.

Wet-mix macadam

The official specification for wet-mix requires that the material be graded down from a maximum size of 40 mm (1½ in) and to contain about 30 per cent of fines (passing 3 mm (⅛ in) sieve) and that the fines should be non-plastic (22). This aggregate is mixed with a pre-determined quantity of water in a conventional plant-mixer. Figure 4.1 shows the appearance of the surface of a well-compacted, wet-mix road base of blastfurnace air-cooled slag. Wet-mix is permitted according to Road Note 29 in the base of all roads for any traffic intensities (38). The results from two major full-scale road experiments of the Road Research Laboratory show slag wet-mix macadam to be a particularly good material for road bases. These are the 1956 experiment on the Retford By-pass in Nottinghamshire, and the 1957 Alconbury Hill experiment on the A1 in Huntingdonshire. The Retford By-pass experiment had the object of studying the relative merits of the different aggregates when used for the construction of granular road bases, with special reference to ease of laying and compaction and to costs and rates of progress of construction. The following extract from a paper by C. D. Grainger (39), is appropriate:

Fibres produced from silica compounds have the advantage that they are immune from pests that attack organic materials, they are resistant to atmospheric oxidation and other ageing factors, and are completely incombustible. They will not support any form of life, fungal, bacterial, or animal, and they are non-hygroscopic.

Slag wool was first manufactured in Wales as early as 1840, and then in America at Cleveland, Ohio, in 1888. The commercial industry started in Great Britain, America and Germany between 1890 and 1910. In America, the annual production in 1928 was 50 000 tonnes; now it is about 400 000 tonnes. In Great Britain, present-day production is about 65 000 tonnes. As the demand for improved heat insulation in buildings increases in this country some increase in this production figure may be expected.

The method of producing slag wool varies between different works, but in general the process involves the melting of slag in a furnace of the cupola type. The molten slag is drawn through a tapping hole and the stream of slag is made to pass in front of a jet of air or dry steam which disperses the fluid slag into a cone of liquid globules. These are drawn out by air resistance to their flight into long fibres. The fibres are sucked into a chamber and the fibrous material laid uniformly on a continuous transport belt. The charge fed into the cupola consists of layers of slag, to which are added small quantities of limestone and silica.

The latest development in the fibre-producing technique is the use of centrifugal machines. The molten slag either falls on to a high-speed spinning disc or is drawn through a high-speed perforated disc, and the fine streams produced are subjected to jets of hot gases forced through nozzles placed around the periphery of the rotor.

It is claimed that fibres produced in this way can have a diameter under one micrometre, and losses arising from premature cooling of particles that are not drawn into fibres are reduced to a very low percentage. However, there is an optimum diameter of fibre, between 2 and 7 micrometres, which enables a desirable volume of air to be entrapped within the packed fibre, and which produces a material that can be easily handled. The length of the fibre is also important, the longer fibres giving a more resilient product which is less liable to disintegration under vibration.

For insulation purposes, slag wool is available in a loose pelleted form as an insulating mat or blanket, as a rigid or semi-rigid slab or as moulded sections for pipes.

The insulation efficiency of slag wool matting that has a density of about 64 kg/m^3 (4 lb/ft^3) may be assessed in terms of thermal conductivity (K) as 0.036 W/m °C (0.25 Btu/ft h °C). The K value for brickwork is about 1.15 (8), for normal concrete about 1.4 (10), and for foamed slag concrete about 0.18 (1.25).

When used for roof-insulating purposes, a 5 cm (2in) layer of slag wool matting laid between the ceiling joints will reduce the heat loss through the roof by nearly 80 per cent and give a thermal transmission coefficient (U value)of 0.10. This is the value required for American and Canadian domestic buildings.

4.8 Modified slag—Slagceram

Blastfurnace slag is either a crystalline material, crystallization taking place as the molten slag solidifies at a relatively slow rate as a result of air-cooling, or it is a non-crystalline glass-type material which has solidified so rapidly under rapid cooling that crystals have no time to form.

The conditions of cooling of air-cooled slag are such that the crystallization process is, in relation to modern technical processes, virtually uncontrolled. As already mentioned, the material so produced, although very satisfactory for specific purposes, has a non-uniform macrocrystal structure, and it usually contains a large quantity of entrapped gas bubbles causing it to be relatively light. Work carried out in Russia and described in a paper which appeared in 1961 (56) showed that it is possible to convert blastfurnace slag into a highly dense, non-porous, microcrystalline material by a process similar in principle to that used for the production of glass ceramics. This process consists of converting the slag into a crude type of glass by the addition of siliceous sand and a nucleating agent, and subjecting the solid glass to a heat treatment (slightly above the annealing temperature) which promotes the growth of micro-crystals from the centres of nucleation. The British Iron and Steel Research Association (BISRA) has carried out further research on the subject and has succeeded in developing the process on a semi-pilot scale for the production of what it has called *Slagceram* (57). The material is cast in moulds to give the required shape, after which it is given the heat treatment. The heat treatment is crucial for success and must be carefully controlled in order to produce the desired crystal structure and physical properties.

Slagceram possesses most interesting properties, and although it has not yet been produced commercially, BISRA suggest that it could most probably be used to advantage in the field of civil engineering. For example, among the various properties quoted by BISRA, attention might be drawn to the following:

Crushing strength	200 MN/m^2 (30 000 lbf/in^2) for a standard 7.5 cm (3 in) cube.
Modulus of rupture	138 MN/m^2 (20 000 lbf/in^2) obtained in a simple four-point loading
Specific gravity	3.0
Scratch hardness	Mohs scale 8–9 (i.e. between topaz and corundum)

Highly resistant to weather and to chemicals.

Reference 2

4. L. V. Fedorova and L. L. Mirskikh, Ref. Information Series, "Utilization of Wastes and By-Products in the Manufacture of Structural Materials and Products" [in Russian], Vol. 7, VNIIÉSM (1981), p. 9.

USING ELECTROFURNACE SLAG FOR MAKING SLAG-CERAMIC

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UDC 666.263.2

The development of highly useful materials based on industrial wastes and secondary raw material is among the most important problems of the domestic economy. At the present time the industrial technology of manufacturing glass crystalline material (sheet slag ceramic and pressed slag ceramic tiles) based on the wastes of ferrous metallurgy, the blast furnace slag, has been adopted. The physicochemical properties of the slag ceramic permit its use in various branches of industry. Thus increased chemical and abrasive stability makes it possible to use slag ceramic to protect equipment from corrosion and abrasive wear in the chemical and mining industry as well as in the manufacture of structural materials [1].

At the Scientific-Research Institute for Automobile Glass glasses for manufacturing slag ceramics have been synthesized from the electrofurnace slags of the Bezhitskii Steel Casting Plant. Compared to the blast furnace slag the electric furnace slag has a higher content of silicon, iron, and manganese oxides and a lower content of calcium and aluminum oxides and also contains metal sulfides.

From the data in Table 1 it is evident that when using electric furnace slag it is expedient to make glasses which crystallize during thermal treatment with the precipitation of wollastonite in the same way that this occurs during the crystallization of industrial glasses based on blast furnace slag.

As the result of an analysis of the literature sources [2] the expediency became evident to develop a glass based on the electric furnace slag in the SiO_2–CaO–MgO system in the crystallization field of pyroxenes. We considered using FeO and MnO as elements replacing the magnesium and calcium oxides in the crystalline lattice of the pyroxene in keeping the electrostatic balance of the valencies. In glasses with the pyroxene composition the replacement of CaO by MnO in amounts to 35% by weight has almost no effect on the formation of the monomineral phase [3], and when MgO is replaced by MnO in the range of 15-45% a polymineral crystalline phase is formed during thermal treatment. Probably this is true also when CaO and MgO are replaced by FeO.

Thus to make glass based on electric furnace slag, the SiO_2–CaO–MgO system was selected in which, when the glass compositions were synthesized in the crystallization field of pyroxenes, the CaO and MgO were replaced by FeO and MnO. The total wt.% of FeO and MnO in the glasses was 14.5%. At such a content of manganese and iron oxides in the glass, the amount of electric furnace slag in the charge was 55-65%. The addition of a larger quantity of manganese and iron oxides to the glass composition impaired the technological properties of the glass.

The glasses were melted in corundum and quartz crucibles at 1500°C. The glasses were thoroughly melted and fired. The fired samples were crystallized in Silit furnaces in a two-

TABLE 1

Slag	Composition, wt.%												
	SiO_2	Al_2O_3	FeO	CaO	MgO	MnO	K_2O	Na_2O	TiO_2	Fe_2O_3	SO_3	S^{2-}	Cr_2O_3
Blast furnace	34,44	11,06	0.29	45.67	2,99	0,34	0,58	0,68	0,49	—	—	1,28	—
Electric furnace	51,40	5,42	9,0	10,96	5,82	13,20	0,28	0,45	0,22	2,15	0,27	—	0,86

Scientific-Research Institute for Automobile Glass, and Bezhitskii Steel Casting Plant.
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step regime which insured full crystallization of the glass with a minimum time of thermal treatment. At the completion of crystallization the samples when fractured had a dense homogeneous microcrystalline structure. The color of the material was brownish. The crystalline phase was made up of compounds of a crystallochemical dioxide group.

It was established that the glass composition BÉ-53 into whose charge 55.47% electric furnace slag was added possesses the best physicomechanical and technological properties in the investigated region.

The BÉ-53 glass composition was melted in semiindustrial conditions in a 170 liter chamotte pot. A pot furnace was used; the melting temperature was 1490 ± 10°C. The charge was loaded in 30 kg portions at 1-h intervals.

The glass melt was fined in 5 h at 1520 ± 10°C. At 1450 ± 10°C the melt was made into tiles 250 × 250 × 20 mm in dimensions and fired at 650°C for 1 h.

The tiles were crystallized at 770°C with a 1-h hold at the crystallizing temperature. The tiles after crystallization were not deformed; they had a dense homogeneous microcrystalline structure. The color of the material was brownish.

Properties of the BÉ-53 Slag Ceramic

Transverse bend strength, MPa	58
Compression strength, MPa	501
Specific impact ductility, kJ/m^2	2.6
Microhardness, MPa	6573
Density, tons/m^3	2.706
Thermal coefficient of linear expansion $\alpha \times 10^7$, °C at	
35-375°C	73.5
375-579°C	98.5
Thermal stability, °C	421
Chemical stability, %	
in concentrated H_2SO_4	99.70
in 35% NaOH	83.46

Semiindustrial tests of the BÉ-53 glass composition substantiated the feasibility of organizing the production of slag ceramic in the form of sheet material and pressed tile with the utilization of electric furnace slag as raw material.

On the basis of the studies conducted by the State Planning Institute of the Glass Industry, the technicoeconomical basis for the organization of the slag ceramic production at the Bezhitskii Steel Casting Plant was developed. The technicoeconomical indices of the designed works for the slag ceramics substantiate the economical expediency of organizing the production of slag ceramic based on electric furnace slag. The annual profit from establishing the production is 1,527,000 rubles.

The developed slag ceramic can be used for inside and outside facing of walls, for floor coverings of homes and industrial buildings, and also to protect equipment working in aggressive media.

LITERATURE CITED

1. Slag Ceramics [in Russian], Stroiizdat, Moscow (1970).
2. D. S. Belyankin, V. V. Lapin, and N. A. Toropov, Physico-Chemical Systems In Silicate Technology [in Russian], Promstroiizdat, Moscow (1954); O. K. Botvinkin, Physical Chemistry of Silicates [in Russian], Promstroiizdat, Moscow (1955).
3. L. A. Zhunina, M. I. Kuz'menkov, and V. N. Yaglov, Pyroxene Ceramics [in Russian], Beloruss. Gos. Univ., Minsk (1974).

Reference 3

SODIUM SULFATE WASTE FOR MAKING SLAG-SITALL TILES

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UDC 666.263.2

Natural sodium sulfate is used in the production of slag-sitall tiles as a means of introducing sodium oxides. Recently the chemical industry has been processing sodium-sulfate waste of the following composition (weight %): 77.89 Na_2SO_4, 17.96 Na_2CO_3, 0.073 Al_2O_3, 0.117 Fe_2O_3, 0.10 $MgSO_4$, 0.23 $CaSO_4$, 0.84 NaCl, 0.75 Na_2S, 1.377 loss on ignition, 0.67 residue insoluble in HCl.

In making glasses for white slag-sitall tiles, the alkali oxides were added to the batch in the form of sodium sulfate waste instead of natural sulfate. The glass was melted in a crucible furnace in 2-liter fireclay crucibles at a maximum temperature of 1450°C for 2 h. For comparison, crucibles were simultaneously placed in the furnace containing batch based on sodium sulfate waste, and also natural sulfate. There was no special difference in the meltings.

The glass so melted was used to cast tiles measuring 120 × 25 × 10 mm which were annealed in a muffle at 650°C for 1 h. The tiles of both compositions after annealing had a brown color with opalescence; after crystallization at 950°C — they were white in color and had a uniform microcrystalline structure.

A test batch was melted in a single-pot furnace in the experimental shop with a pot capacity of 170 liters. The melting temperature was 1530°C. Fining was done at 1540°C, and working at 1450°C. Tiles measuring 250 × 250 × 15 mm were made from the glass.

During working the viscosity of the glass was: at 1300°C 180 dPa·sec, at 1200°C — 548 dPa·sec. The minimum viscosity measured with a dynamic heating system at a rate of 115°C/h, shows that the glass crystallizes during heating and the minimal logarithm of viscosity at 50°C is log η = 9.40 (Fig. 1).

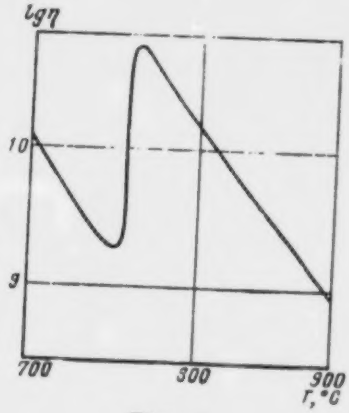

Fig. 1

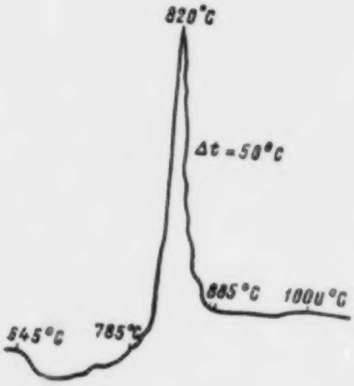

Fig. 2

Fig. 1. Change in viscosity of glass based on sodium sulfate waste in the crystallization temperature range.

Fig. 2. Differential thermal curve for the crystallization of glass based on sodium sulfate waste.

Scientific-Research Institute of Automobile Glass. Translated from Steklo i Keramika, No. 7, pp. 3–4, July, 1981.

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TABLE 1

Factors	Slag-sitall tile	
	with natural sodium sulfate	with sodium sulfate waste
Strength, MPa:		
transverse bending	42,9–50,5	91–126
compressive	788,5	741
Microhardness, MPa	5,970	6,375
Loss of weight on abrasion, kg/m^2	0,125	0,135
Density g/cm^3	2,635	2,694
Temperature coefficient of linear expansion $\alpha \cdot 10^{-7}$ °C in the range, °C		
60...642	86	Not det.
48...396	Not det.	75,4
396...568	»	94,5
560...600	»	122,8
Thermal-shock resistance °C	»	280
Chemical resistance, % to:		
concentrated sulfuric acid	99,82	99,97
35% NaOH	82,28	81,25

The differential-thermal analysis curve for the crystallizing glass based on waste has one exothermic effect at 820°C (Fig. 2), which is explained by the rapid crystallization of the glass. DTA data was used to determine the crystallization schedule for the goods.

Crystallization of articles was done in double-staged cycle soaking for 1 h at 650°C with subsequent increase in temperature to 950°C. After crystallization the articles had a dense uniform microcrystalline structure, while in color. There was no deformation.

The physicochemical and mechanical properties of the slag-sitall tiles are shown in Table 1.

Thus, the slag-sitall tiles made from sodium sulfate waste are as good as those obtained with natural sodium sulfate. The savings from the use of such waste instead of natural in the production of slag-sitall tiles white in color for a volume of 460,000 m^2 per annum is 67,900 rubles.

Reference 4

the same channel height. Because of this in the preheat and firing zone a relatively low coefficient of nonuniformity of temperature distribution, 1.54 (Table 3), is obtained; this made it possible to fire up to 500-mm ameter sewage pipes (the firing time was 32 h).

For the preheat and firing zones very high values are characteristic for the coefficients of nonuniformity of temperature distribution in comparison with the cooling zone (especially for furnaces with a high channel ight), which must be considered in selecting the length of these zones. The following are recommended for e ratio of the length of the preheat and firing zones to the total furnace length: for firing sanitary products, 50-54%; for sewage pipes, 54-58%; and for acid supports, 58-62%.

Thus, the coefficients of nonuniformity of temperature distribution must be considered in the selection of firing time. This permits the operation of the tunnel furnaces to be increased and the quality of the products to be improved.

USING BLAST-FURNACE SLAG IN CERAMIC MELTS

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UDC 666.3.004.8

The multiple use of raw materials is a real problem in developing the national economy of the USSR. One of the promising directions in the solution of this problem is utilizing in structural materials technology e wastes of different industrial branches, among them the metallurgical branch.

Ceramic melts based on hydromicaceous-kaolinite clay and blast-furnace slag were studied. This was cause the clays of the mentioned mineralogical type are most widely used in ceramic technology, and the chnology developed by the Scientific Research Institute for Structural Materials Industry for making the granulated slag has been effectively adopted by the largest metallurgical enterprises [1].

The experimental melts were made by the slip method: by wet grinding the components in a ball mill to fineness determined by a residue of 2-3% on sieve No. 006 followed by drying to a 6-7% moisture content and grinding to a particle size not greater than 2 mm. Samples of the products, among them the melt based on the slag without additions, were made by semidry pressing at a pressure of 24 MPa. The samples were dried to residual moisture content of 0.3-0.5% and were fired according to two schedules: a long 24-h schedule with maximum temperature range of 950-1300°C and a 50-min accelerated schedule in the roller furnaces at maximum temperatures of 960 and 1040°C.

The chemical analysis of the raw material (Table 1) showed that the Krivorozh blast-furnace slag has a high CaO content and a low Al_2O_3 content as well as a high amount of MgO and the presence of sulfur in the form of RS type sulfides. The phase-mineralogical composition of the slag (Fig. 1) contains $3CaO \cdot Al_2O_3$ crystals, calcium silicate $\alpha 2CaO \cdot SiO_2$, bredigite $\alpha 2CaO \cdot SiO_2$, and a glass phase. The Popasnyan and the Novorai ays belong to the refractory hydromicaceous-kaolinite clays.

The obtained experimental data indicate a significant difference in the sintering parameters [2] in the mples of the blast-furnace slag and the hydromicaceous-kaolinite clay. The slag samples have a low density

TABLE 1

Raw materials	Composition, wt. %											
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	MnO	S	SO_3	Na_2O	K_2O	calcination loss
Krivorozh blast furnace slag	40.03	8.65	0.71	0.25	43.16	4.08	0.72	1.66	—	0.43	0.54	—
Clay:												
Popasnyan	62.88	22.80	2.32	1.06	0.68	0.68	—	—	0.26	0.25	1.65	7.29
Novorai	55.67	29.65	1.23	0.70	0.49	0.71	—	—	0.10	0.50	1.54	8.79

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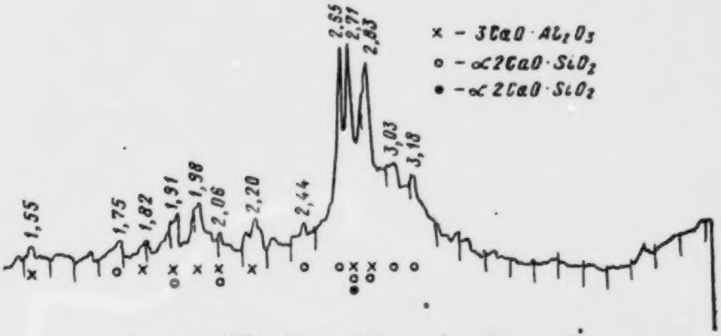

Fig. 1. Diffraction pattern of a slag probe.

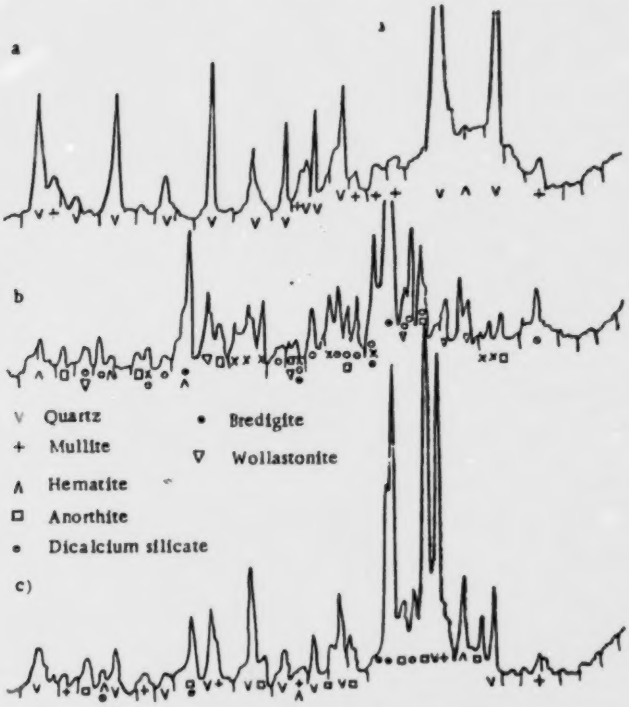

Fig. 2. Diffraction patterns of samples from experimental melts after a rapid firing at 1040°C. a) Hydromicaceous-kaolinite Popasnyan clay; b) Krivorozh blast-furnace slag; c) melt with a slag-to-clay ratio of 1:1.

(1.7-1.79 g/cm³) at a maximum firing temperature of 950-1000°C. With an increase in the firing temperature to 1200°C their density does not change, and at 1250°C the samples begin to melt and are deformed. The Popasnyan clay samples have a uniform density (from 1.82 to 2.39 g/cm³) at a maximum firing temperature of 950-1150°C. Upon increasing the temperature to 1250°C their density does not change, and at 1300°C signs of buckling are noticed. The sintering parameters of the Novorai clay are close to those of the Popasnyan clay but the maximum density of the Novorai clay is attained at 1200°C.

At the maximum density in the firing temperature range of 1000-1200°C the slag samples are characterized by high water absorption (22-23%) and a low bend strength (4-9.5 MPa), and the Popasnyan clay samples at maximum density in the temperature range of 1150-1250°C have a low water absorption (0.4-1.4%) and a high bend strength (34-36 MPa). It should be noted that in the maximum firing temperature range (950-1150°C) the slag samples practically do not shrink; their linear expansion (shrinkage) value is in the range from +0.2 to −0.7%. For the clay samples an important shrinkage is noticed increasing from −1.2 to −8.2%.

TABLE 2

Index of the melt	Composition, wt. %		Sample properties after accelerated firing of the melt							
			960°C				1010°C			
	blast-furnace slag	Popasnyan clay	shrinkage, expansion, %	water absorption, %	density, g/cm³	bend strength, MPa	shrinkage expansion, %	water absorption, %	density, g/cm³	bend strength, MPa
TS	100	—	+0.6	20.4	1.67	5.0	+0.7	26.3	1.61	6.0
TS1	75	25	−0.2	18.3	1.75	19.5	+0.1	19.3	1.75	14.0
TS2	50	50	−1.9	13.4	1.92	28.5	−1.5	13.2	1.90	23.5
TS3	25	75	−2.6	13.4	1.92	23.5	−2.6	10.0	1.98	26.5
B181	—	100	−2.7	13.3	1.93	18.5	−4.2	10.1	2.06	20.5

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* Expansion is indicated by the plus sign; shrinkage by the minus sign.

During the accelerated firing at 960 and 1040°C (Table 2) the slag samples are also characterized by low int ing and a correspondingly high water absorption and low strength. However, utilization of a charge based blast-furnace slag and hydromicaceous-kaolinite clay permits sintering to be increased and the physico-ec nical indices of the samples to be improved.

During the firing in the roller furnace at 1040°C, the samples from melts TS2 and TS3 have two times ss shrinkage than the samples from the clay B181 at the same water absorption.

The increase in strength and decrease in shrinkage of the calcined samples of the melts based on clay d ast-furnace slag are due to the peculiarities of their phase composition. X-ray structural analysis of e samples conducted on the URS-50IM diffractometer established the intensive synthesis of anorthite crystals aO $l_2O_3 \cdot 2SiO_2$ during the firing (including the accelerated) of melts based on clay and slag (Fig. 2). The ea st degree of anorthite formation is observed at a ratio of slag to clay equal to 1:1 (samples from the TS2 elt).

t is evident that during the firing of hydromicaceous-kaolinite clay, the anorthite does not form, and ri the firing of the slag samples, an insignificant amount forms. Consequently, the optimum ratios found r calcium, aluminum, and silicon have an effect on accelerating the formation of anorthite.

The possibility of synthesizing anorthite from melts based on clay and blast-furnace slag have practical lu or obtaining and regulating the properties of structural and technical ceramics [3].

The values of shrinkage, water absorption, and strength obtained during rapid firing for samples from e 2 and TS3 melts containing 25-50% blast-furnace slag indicate the possibility of utilizing these melts for an cturing unglazed facade plates with a colored body.

To determine the optimum melt composition which insures the required degree of sintering of the plate ri a rapid firing and a water absorption of not more than 10%, the method for mathematical planning of an pe ment [4] must be used. By utilizing an orthogonal plan of the second order the following melt composi-n (in weight percent, %) was established: 75 hydromicaceous-kaolinite clay, 15 blast-furnace slag, 5 glass ra and 5 nepheline concentrate.

The plates from the developed melt had a bright gray color after firing. To obtain plates of bright-red, e, green, gray, and dark-gray colors, 6% pyrite cinders, 6% Co_2O_3, 6% Cr_2O_3, 6% MnO_2, and 4% MnO_2 + rite cinders were added additionally (over 100%) to the indicated composition, respectively.

From the developed melt with the coloring additions and without them 120 × 65 × 7 mm plates are ob-ned with a rapid firing in the commercial roller furnace of the Kiev Factory Keramik at 1020–1040°C for m ; they have rather high physicomechanical indices (water absorption, 6-9%; bend strength, 30-40 MPa; si nce to frost, more than 35 cycles) which meets the requirements of GOST 13996-77.

Applying the investigation results permits the wastes of the metallurgical industry to be used (blast-fur-ce ag in the ceramic technology) and the consumption of glass scrap and nepheline concentrate to be de-ea d; these can be used as flux in the production of ceramic plates.

LITERATURE CITED

. S. Grigor'ev et al., in: Structural Materials, Parts, and Products [in Russian], Budivel'nik, Kiev (1968), p. 140.

Reference 5

ABRASIVE WEAR OF GLASS ENAMELS AND SLAG SITALL USED IN HEAT ENERGETICS

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UDC 666.293:621.133.7

In recent years glass enamels have been used in thermal power stations as coatings to protect from corrosion the packing of regenerative auxiliary air heaters and components of the air-heater pipe system. In addition, slag sitall and ceramic are being more and more widely used as design materials in their own right. The need to use materials of this type is the result of the intense sulfuric acid corrosion of metal parts of the back end equipment of boiler assemblies operated on liquid or solid, sulfur-containing fuel.

When coal is burned in thin boilers, the hot flue gas passing through the air heaters contains a large amount of ash particles which have a strong abrasive action on parts protected by glass-enamel coatings or made from ceramic or slag-sitall. Therefore, it is most important to evaluate the resistance of these materials to abrasive wear.

In order to determine the abrasion-resistance of the coatings we used a method involving the free fall of an abrasive [1]. We studied the effect of the temperature of the enamel and the angle of attack of the abrasive stream on the wear-resistance of the A-20 coating. The method used to plan the experiment was a second-order orthogonal central composite plan. The angle of attack α was varied from 15 to 45° and the temperature t from 100 to 300°C.

After processing the experimental data we obtained a mathematical model associating the rate of wear $B[g/(h \cdot m^2)]$ of the coating and the parameters α and t as follows:

$$B = 0.01\,t + 0.42\,\alpha - 0.0008\,\alpha\,t - 5.58.$$

As would be expected, the angle of attack has a greater effect on the extent of the wear than the temperature of the coating. Thus, when the angle of attack is changed from 15 to 45°C, the rate of wear increases by approximately an order of magnitude while an increase in temperature from 100 to 300°C reduces the wear only 1.5-2-fold. The temperature of the coating has a significant effect on the wear of specimens with an angle of attack greater than 35-40°. With small values of α, the intensity of the wear on the coating is virtually independent of the temperature. A reduction in the rate of wear with an increase in temperature within the experimental limits is clearly associated with the emergence of a plastic mechanism of destruction which requires a higher expenditure of energy than that of brittle fracture.

It was established as a result of the tests that abrasive wear (mg/kg) of enamel coatings A-20, 20/8, and 25 without a primer used to protect the packing of regenerative air-coolers was 1.6, 1.2, and 1.6, respectively; for the coatings 13-III and 18 used for the protection of the main pipework of the air heaters it was 1.6 and 2.9; the chemical apparatus coatings LK-1, 261, 1513-Ts, and N-24 had abrasive wear of 15, 1.9, 2.6, and 1.2, respectively. The abrasive wear of slag sitall intended for the manufacture of the packing for the TÉS regenerative air heaters was 0.3 mg/kg. The tests were carried out at room temperature; the consumption of abrasive was 5.5 kg/h; the height of the drop was 1200 mm; the angle of attack, 45°; and the tests lasted 9 h.

It is clear that the most wear-resistant coatings are the 20/8 and N-24. The resistance to wear of the A-20, 25, and 13-III coatings are ~30% lower. The lowest wear resistance is found in the 1513-Ts and, particularly, in the 18.

The slag sitall from the Avtosteklo Plant has a very high wear resistance; the abrasive wear was a quarter of that of the best enamel coatings. We can therefore recommend the wide

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Southern Branch of the F. E. Dzerzhinskii All-Union Technological Institute. Translated from Steklo i Keramika, No. 6, p. 14, June, 1983. "Glass & Ceramics" - Plenum

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use of this material as a design material in the back end equipment oi boiler aggregates designed for use with a high-ash fuel, particularly in the eastern regions of the USSR.

LITERATURE CITED

1. G. V. Basayants, V. A. Svetlichnyi, et al., Steklo Keram., No. 1, 16 (1982).

INFLUENCE OF ALKALIS ON THE PROPERTIES OF WATER SUSPENSIONS OF FUSED QUARTZ AND CASTING MADE FROM THEM

V. A. Bevz

UDC 666.192:66.063.6

One method of obtaining unfired quartz ceramics, which involves activating the contact bonds, specifies the introduction of alkali oxides, which significantly increase the solubi ity of the surface of the particle of fused quartz and, as a result, the degree of strengthe ing of the semifinished article [1, 2].

Alkali oxides are also added to ceramic materials of this type to accelerate bulk crystallization during heating in the production of cristobalite ceramics [3, 4]. In some cas the opaque fused glass itself is contaminated with alkali impurities.

The strongest and densest articles are obtained by slip casting highly concentrated slips. The alkali oxides can be introduced by impregnating the dried casting with alkali solutions, but it is more economical to incorporate the alkali elements when preparing the slip. Previously [5, 6] reference was made to the effect of NH_4OH additions on the properties of fused quartz suspensions, and on the porosity of the castings made from them. Small additions used in this case increased the pH values to 8-9.

This paper gives the results of a study of the properties of water suspension of fused quartz with pH values of up to 12, and also blanks and specimens of unfired quartz ceramics obtained from them. The alkali additives consisted of water glass, potassium and sodium hydroxide, silicone liquids GKZh-10 and GKZh-11, solutions of sodium carbonate, and ammonia. These substances were chosen because ordinary fused quartz castings, after storage in water solutions of the above alkalis, followed by thermal-moisture treatment, acquire the highest strength. It is sufficient in this case to add 0.005-0.2% alkali based on R_2O to the casti with the solution. Alkali calculated on the basis of solids was added in the same amount t the suspension.

It was important during the research to decide the stage at which the alkali should be added. All attempts to obtain fused quartz slip with good casting properties by milling in an alkali medium with pH values of 9.6-11.8 proved unsuccessful.

Adding the alkali to the suspension after grinding is complete increases the density and strength of the castings. The best properties were obtained by adding the alkali to the unstabilized suspensions, followed by stabilization through mixing. There was also a reduction in the time needed to obtain the suspension, since adding the alkalis to the stabilized suspension requires a second gravitational mixing.

Figure 1 shows the relationship between the properties of the unstabilized suspension containing 28% particles with sizes of up to 5 μm and 3.5% above 63 μm, with an addition of water glass and without it, and also the properties of castings from the same suspensions against the stabilization time when mixing was done at the initial stage. The pH value of the slip was hardly altered even with a stabilization period of 80-120 h. For other types of additive the overall nature of the relationships is similar to the above. Despite the high viscosity of the suspension with alkali additions in some cases, the castings' porosit is 1-1.5% lower. The strength of the dried castings is 3-5 times higher than for castings made from ordinary suspensions, and for castings subjected to thermal-moisture treatment it

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Reference 6

Slagceram, A New Constructional Material

By S. Klemantaski and B. Kerrison

(British Iron and Steel Research Association)

(Based on a Lecture delivered to the Road & Building Materials Group of the Society of Chemical Industry on October 21, 1966)

The British Iron and Steel Research Association have developed a constructional material provisionally called slagceram, made by the controlled crystallisation of a slag-based glass. Production has reached a pilot-plant scale, a first evaluation of the properties of the material has been made, and the mechanisms involved in the production process have been studied.

Introduction

The present paper is based on a lecture given in October 1965 to the Road and Building Materials Group of the Society of Chemical Industry. It will be followed in due course by a comprehensive definitive paper.

The object of most metallurgical operations is to purify. Some of the impurities leave as gases, others form molten liquids, generally by combining with materials (fluxes) specially added for the purpose. These molten liquids are called slags and in many ways resemble molten rock.

The greatest mass of slags is produced by the steel industry, and it is with a new constructional material, slagceram, based on steel-industry slags, that this paper deals. The development of slagceram by the British Iron and Steel Research Association (BISRA) has involved a considerable research and testing effort.

As a background to the account of slagceram an outline of the nature of slags and their present methods of processing and fields of use will be given first.

In the steel industry there are two main groups of slags:

(1) blast-furnace slags, which arise in the production of the high-carbon iron alloy called pig iron;

(2) steelmaking slags, which arise in the subsequent conversion of this alloy to the purer form of iron, called steel.

The approximate composition ranges of slags and related substances, including some slagcerams, are shown in Fig. 1 in terms of three major components.

The bulk of steelmaking slags made in the UK have generally found a ready and reasonably profitable market, and there has therefore been comparatively little incentive to find new uses for steelmaking slags.

Blast-furnace slags in the UK often have to compete with plentiful alternative materials. They are used mainly in the air-cooled form, usually produced by tipping the molten slag from the ladles in which it leaves the blast-furnace plant into pits or down banks, llowing it to cool relatively slowly, and digging it out. A small amount is made by leaving the slag to cool in the ladle. With either procedure the products are mostly crushed and screened. The slow cooling with hese air-cooled slags gives time for crystallisation to o far towards completion, but there is little control over the size, size uniformity or nature of the crystals.

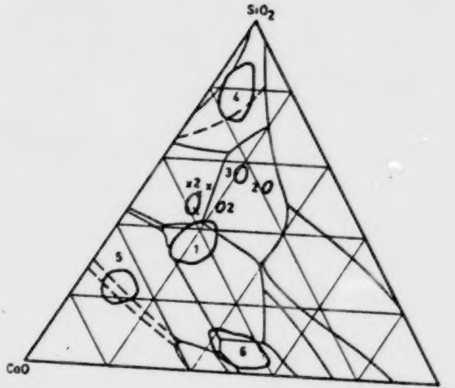

FIG. 1.—*Compositions of slags, slagcerams and related substances*

1. Basic BF slag
2. Acid BF slag
3. Copper slag
4. Commercial glass
5. Portland cement clinker
6. High-alumina content
X. Slagcerams

A relatively small amount of slag in the UK is treated, while molten, with air/steam/water mixtures to give foamed slag, a light material used, for example, as the aggregate in light-weight concrete. The cooling in such processes is much quicker than in air cooling but, even so, the foamed slag usually contains little glassy material.

Most blast furnace slags show useful hydraulic (*i.e.* cement-like) properties in the glassy state. This is produced by the very rapid cooling obtained when the molten slag is treated with a large excess of water, which has the dual effect of breaking the slag up into small particles and cooling them.

A feature of all the applications mentioned above is that they involve a reassembly of particles made by the breakdown of large masses of slag. For example, in light-weight concrete panels the foamed-slag aggregate has been cemented together; in road surfaces the crushed slag has been bonded together with, for example, bitumen. This subdivision and reassembly is avoided if molten slag is formed directly into the final articles (*e.g.* cobbles and kerbstones), but comparatively little use has been made of this technique. This comparative neglect is due partly to market limitations for formed slag products, but also to technical difficulties of which the long annealing needed for satisfactory products is an important one.

BISRA have for many years taken part in the search for new and better methods of slag utilisation and slag products. More recently it was decided to pay greater attention to higher-value products that could accommodate reasonable conversion costs and at the same time account for a large quantity of slag.

The most fruitful approach has proved to be the one, comparatively neglected in the UK, of making the slag into glass and producing from it articles for a tonnage market, the building trade for example. This approach, taken a stage further, has led to the development of slagceram, a material produced by the controlled crystallisation of the slag-glass material.* The use of controlled crystallisation brings slagceram into the general class of glass ceramics.

The slagceram development work was taken in the laboratory up to a scale of production with melts of up to 20 lb. Pilot-plant work, on a hundredweights scale, was then started with the primary object of producing materials for evaluation and demonstration in reasonable quantities. More recently, the emphasis in the pilot-plant work has shifted towards process development and collaboration with companies potentially interested in slagceram production and use. The pilot-plant work is supported by laboratory special investigations to explore process and product modifications. Laboratory work on the more fundamental aspects of slagcerams and their production continues, and fundamental work is also being sponsored at universities. A comprehensive testing programme is being carried out on the material by outside bodies, and test panels of the pilot-plant material have been placed (*e.g.* in chutes and floors).

Slagceram Production

A—*Basic Theory*

Glass ceramics are produced by the almost complete crystallisation of a body made from a special glass. In a way, this process may be regarded as the opposite of that for the production of ordinary ceramics, where a body of largely crystalline particles is heated until enough glass is produced to bind the particles together. In the manufacture of ordinary glass, great care is taken to ensure that no crystals from the raw materials either remain or are formed, so glass ceramics are also very different from glass.

Slagceram can be regarded as a new form of glass-ceramic having an exceptionally complex composition and suited to a tonnage market. The basic theory of slagceram production can be conveniently discussed in terms of glass ceramics. Excellent accounts of these materials have been given recently in two books.[2,3]

It is not always easy to prevent the crystallisation of glass because there is generally a considerable driving force for crystallisation. Whether crystallisation in fact occurs depends on factors such as the chemical composition, temperature and the presence of discontinuities, such as the walls of a container or particles distributed in the glass and capable of acting as centres of crystallisation. Such discontinuities, which may be termed mechanical centres of crystallisation, lead to the formation of coarse crystals, probably of random size, and cannot be used for the very fine and uniform crystals needed for the superior properties of glass ceramics. Such crystals can be obtained if the discontinuities are very close together in the glass and the growth of crystals on them starts at about the same time and proceeds at about the same rate.

In the glass-ceramic process this is brought about by two separate operations. In the first, the required high concentration of centres of crystallisation is obtained by allowing discontinuities to develop in the body of the glass as a result of structural changes. These changes involve relatively little movement of atom groups, and the process is carried out by holding the glass at about the annealing temperature. With the special glass composition used, the correct concentration of discontinuities (nuclei) capable of acting as centres of crystallisation in the second stage is obtained, but the glass still is not fluid enough to accommodate the more drastic rearrangement of atoms needed for crystals to grow on these nuclei. This is accomplished in the second stage in which the temperature is raised to a level where the mobility of atoms and atom groups is high enough for crystals to grow on the nuclei. Each of these stages has its temperature range, with some overlap. With increasing temperature the rate of the process in each stage rises to a maximum and then falls away to zero: in the first stage the rate is the number of nuclei being produced per unit volume of glass in unit time; in the second, the rate of growth of crystals. These processes are shown schematically in Fig. 2.

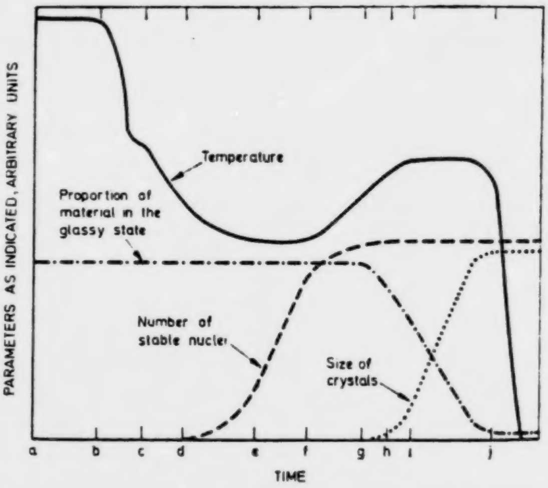

FIG. 2.—*Production of a glass ceramic. Temperature, proportion of material in the glassy state, number of nuclei and size of crystals, shown as functions of time*

In the period a–b the molten glass is being brought to uniformity, in b–c its temperature is reduced to that best for shaping, carried out at c. In c–e the shaped article is being cooled to a temperature giving a large number of nuclei formed in unit time, but without crystallisation. Nucleus formation starts at d and persists to h; after g, when crystal growth starts, the nuclei are increasingly enclosed in crystals. In f–i the article is being heated to a temperature giving a high rate of crystal growth which ceases after j, when the article is being cooled. The material remains virtually entirely glassy until g.

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* A similar material has been produced in the USSR under the trade name "slag sitall"[1].

For various reasons, including the extreme smallness of the nuclei, the first stage, nucleus formation, is difficult to study. Of the various mechanisms recognised, one that is of interest for slagcerams is the formation of nuclei by separation of oxides. For this the composition of the glass is made such that sufficient stress arises in the atomic groups (networks) of the glass at the nucleus-formation temperature for them to break up into groups of two or more types, at least one of which can act as a centre for crystallisation in the second stage. With the silicate-aluminate type of glass in slagceram the introduction into the molten glass of transition-metal oxides can lead to such a process with separated oxide groups forming, as it were, an emulsion within the parent glass. The size of the separated groups is important, since only if they are above a certain critical size will they survive, especially at the higher temperature of the second stage, and be effective. If below, they disappear before they can perform their function of becoming a centre on which crystals can grow.

The second stage starts with a glass that looks unchanged but in fact contains a high concentration of uniformly-distributed nuclei, produced in the first stage. As the temperature is raised, the atomic groups of which the bulk of the glass is made up become freer to move, and the driving force that exists for the glass to crystallise can become effective. With the rather complex composition of the glasses used for glass-ceramic production, and even more so with the more complex compositions for slagceram production, there are many different crystals that could be formed. Since, for the nucleus to be effective there must be a certain minimum similarity between the arrangement of atoms in it and in the crystals, the nature of the nucleus probably has a very considerable effect on which of the different possible crystals are formed.

These crystals are not necessarily those that are the most stable (*i.e.* for whose production there is the greatest driving force) under the particular conditions of the crystallisation process, and are likely to be even more different from those most stable at room temperature. There is some evidence that the superior properties of glass ceramics are associated with the fact that the crystals are not the most stable ones possible.[4]

Solid solutions are often present, which is to be expected, since a crystal whose lattice is more tolerant as regards substituting elements could accommodate a greater variety of the many different atoms in the neighbourhood of the nucleus in a glass of complex composition. The growth of such a crystal would involve less movement of atoms than would the growth of a crystal with a more selective lattice.

In slagcerams the main minerals detected are: diopside ($CaMgSi_2O_6$), and many of its substitution products, wollastonite ($CaSiO_3$), melilites (such as akermanite $Ca_2MgSi_2O_7$) and anorthite ($CaAl_2Si_2O_8$).

The size, nature and uniformity of the crystals have a considerable influence on the properties of slagceram.

The amount of the residual glass is evidently an important factor because, as shown by the example below, it is much weaker and softer than the slagceram obtained from it.

	Glass	*Slagceram*
Rupture strength, thousands of p.s.i.	5·7	22·5
Hardness, Mohs' scale	4½–5½	7½–8½

As regards chemical attack, too, the glass is much weaker, for example, it quickly forms a thick colloidal deposit in dilute acid, whereas the slagceram made from it is hardly affected.

The question of the relation between structure and properties is complicated, involving, among other things, the nature of the crystals themselves, the way they directly interlock with each other, the way they are bonded to the residual glass, the amount and properties of the residual glass, the presence of defects such as pores and cracks, crack propagation.

Little progress has yet been made towards an answer to this question. Among the difficulties are that of measuring precisely the amount of residual glass. Another is to define crystal size, since individual crystals are more often than not concealed in relatively large aggregates (spherulites, dendrites). While this important gap in knowledge undoubtedly hampers progress, sufficient is known for progress to have been made towards the improvement of slagceram properties.

B—*A possible full-scale slagceram production process*

The full-scale production process for slagceram can be envisaged in various ways: one of the more likely ones is given below. This includes the stages of the adjustment of slag composition to give a glass suitable for crystallisation; shaping of the glass into the final (or almost final) article; and two-stage heat treatment of the glass article to convert it into slagceram. These stages, and the associated movement of materials are discussed below. The flow sheet is shown in Fig. 3.

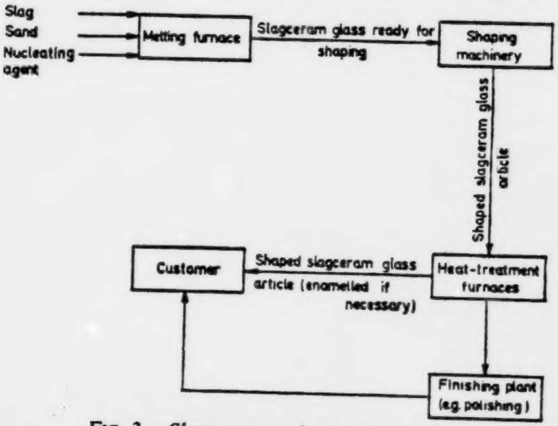
Slag
Sand
Nucleating agent
Melting furnace
Slagceram glass ready for shaping
Shaping machinery
Shaped slagceram glass article
Customer
Shaped slagceram glass article (enamelled if necessary)
Heat-treatment furnaces
Finishing plant (e.g. polishing)

FIG. 3.—*Slagceram production flowsheet*

(a) *Material flow*

The main starting material for slagceram production is slag, which is probably best delivered to the slagceram plant in the molten state, since this not only saves heat in the addition of the other materials but also speeds up their assimilation and thereby saves on plant capital costs. The slagceram plant would probably be sited away from the blast furnaces, and the slag could then be delivered molten in ladles, which is the way most slag is transported at present. The main additive to slag to give a melt of the required composition is silica. The amount needed is, perhaps, 30 parts of silica to 100 of slag. The silica could be in the relatively pure form as sand. The nucleating agent, a minor additive, could be pre-mixed with the siliceous additive, or might even be a part of it.

At each stage in the slagceram production some rejects would arise. Though all the reject material could be returned for remelting, some might be used in a subsidiary production process (*e.g.* cracked glassy articles could be crushed and then given the normal heat treatment to produce a superior aggregate).

(b) *Melting and conditioning*

The melting and mixing of the components to give a homogeneous melt could take place in the types of furnace normally used in glass making. In these furnaces the melt is relatively still. On the other hand, combination of one or several highly turbulent furnaces, where rapid mixing and assimilation would occur, and a final furnace, where the melt could be held to allow bubbles to settle out, might well prove advantageous. For the first furnace an enlarged version of the rotating furnace of the present pilot-plant described in section C, might be very suitable. Alternatively, turbulence could be produced partly or entirely by the action of the flame. The final furnace might well be divided, on the lines of a glass tank, into different zones, in the last of which the melt would be brought to the correct temperature for the shaping operation. Because the relative opacity of the slagceram glass melt hinders heat transfer down from its surface, it would probably be advantageous to supply part of the heat by direct passage of electricity through the melt, and artificial stirring would also help. Both these techniques are used in the glass industry for the relatively opaque coloured glasses. The final zone would end in a feeder or, more probably, a series of feeders in parallel, for dispensing the glass with the right viscosity and at the right rate to the shaping mechanisms.

For foamed slagceram, foaming could be effected at the melting stage; the final furnace would then be omitted or used merely to get the melt to the right temperature. Alternatively, a special foaming operation could be carried out on the melt as part of its final conditioning for shaping.[5] Yet again, foaming could be carried out on the shaped articles.[6]

(c) *Shaping*

The shaping processes used in the glass industry (casting, pressing, rolling, extrusion, drawing and even blowing) would, with suitable modifications to take into account the difference in properties between slagceram and ordinary glasses, be suitable for slagceram glass. One important difference is that slagceram glasses are relatively opaque, and the surfaces of the work during forming would therefore tend to cool much quicker than with the usual transparent glass, in which heat from the inside is radiated to the surface. Another important difference is that the viscosity of the slagceram glass can change with temperature much more sharply than that of ordinary glasses, and the effect of this on the shaping properties of slagceram glass is aggravated by the opacity. It would seem therefore that shaping processes would be carried out at faster rates. The forming temperature could well be over 900°c.

It would be most efficient to make as close an approach to the final shape as possible before heat treatment, but if specially close size control were needed it might be necessary to have a final shaping operation just before crystallisation is complete. For the production of objects such as flat tiles, a continuous ribbon of rolled or drawn slagceram glass could be given diamond scratches and broken, as with sheet glass.

(d) *Heat treatment*

For heat treatment, the usual type of continuous glass-annealing furnace (lehr), modified to give the required times of several hours in each of the stages (formation of nuclei—and crystal growth on them), might well be used. The temperatures envisaged are of the order of 650–750°c (generally near the annealing point) for nucleus formation, and 900–1100°c for crystallisation. The operation would end with the final cooling of the crystallised material (slagceram). Some counter-current process, embracing also the final cooling stage, would certainly give the greatest thermal efficiency for the whole heat treatment process, but may nevertheless prove inexpedient because of complexity and high capital cost.

(e) *Finishing processes*

Though slagceram of different colours can be produced by adjustments of composition and heat treatment conditions, the range of colours is limited. To go beyond this range or to obtain a bright or specially chemically resistant surface, vitreous enamelling can be used. As in some modern glazed-tile production processes, the enamelling could be combined with heat treatment. Enamelling has been carried out on the pilot-plant product without difficulty.

Very attractive polished surfaces can be obtained on slagceram, but its hardness makes this an expensive operation. On the other hand, since slagceram can be produced in thin plates, polished slagceram could still be competitive as a facing material. Other possibilities are mentioned below.

Pilot plant

The pilot-plant at Warrenby (Yorkshire) has some resemblance to the plant envisaged above. Its design was strongly influenced by design parameters already established for glass-making plant. However, because with slagceram glass the viscosity changes sharply with changes in temperature, some modification of glass manufacturing technique has been necessary, especially in the shaping sequence.

Blast-furnace slag, the main constituent of slagceram, is a most complex by-product and includes in its chemical composition practically all the oxides used in the manufacture of glass. The exact proportion of oxides present varies from source to source and, to some extent with time from a given source, but fortunately the slagceram process is not critically controlled by chemical composition alone; and provided that melting conditions are correct, these variations can be tolerated without deterioration of the final product.

Because molten slag has not yet been available, the pilot-plant uses cold ½ in.–¾ in. slag, this being melted with ordinary building sand and the nucleating agent. However, plans are well advanced to use molten slag direct from the blast-furnace as the starting material, and this should result in a decrease in heating costs and time to prepare a given quantity of material. Nucleating agents from various sources in the refined and crude state have been tried, with equally successful results.

Two different melting units are in use, the first being a scaled-down version of a conventional glass-melting tank, and the second an adaptation of modern steel-making practice to glass manufacture.

The miniature glass tank is fired by two gas/air burners. The capacity is 150 lb of molten slagceram glass. The tank is lined throughout with sillimanite bricks but more exotic refractories might be desirable in larger-scale plant, especially at the liquid line.

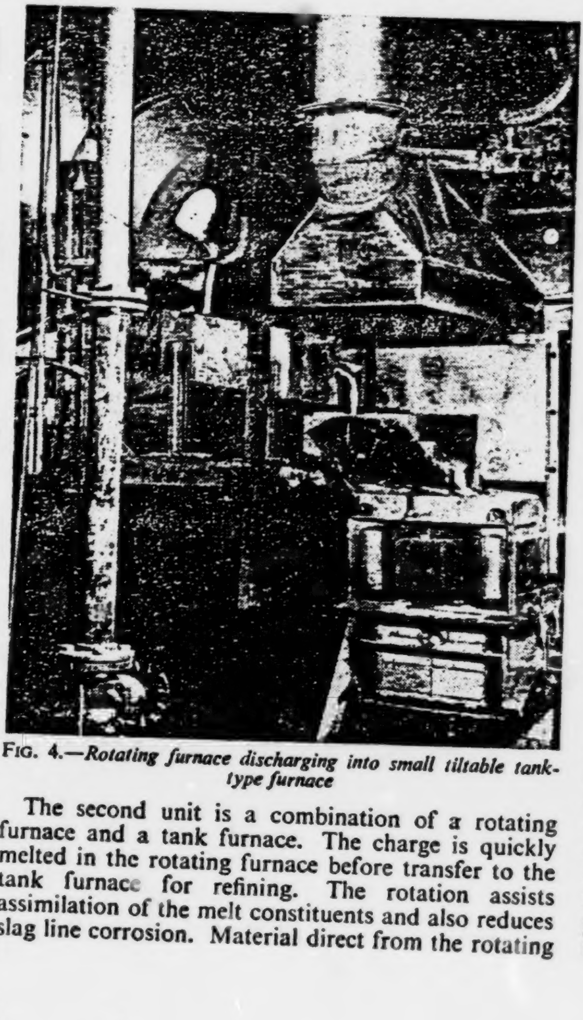

Fig. 4.—*Rotating furnace discharging into small tiltable tank-type furnace*

The second unit is a combination of a rotating furnace and a tank furnace. The charge is quickly melted in the rotating furnace before transfer to the tank furnace for refining. The rotation assists assimilation of the melt constituents and also reduces slag line corrosion. Material direct from the rotating furnace is usually frothy and forms the basis of a method of making foamed slagceram. The rotating furnace is lined with a castable sillimanite refractory and is fired by a high velocity oxygen: propane burner.

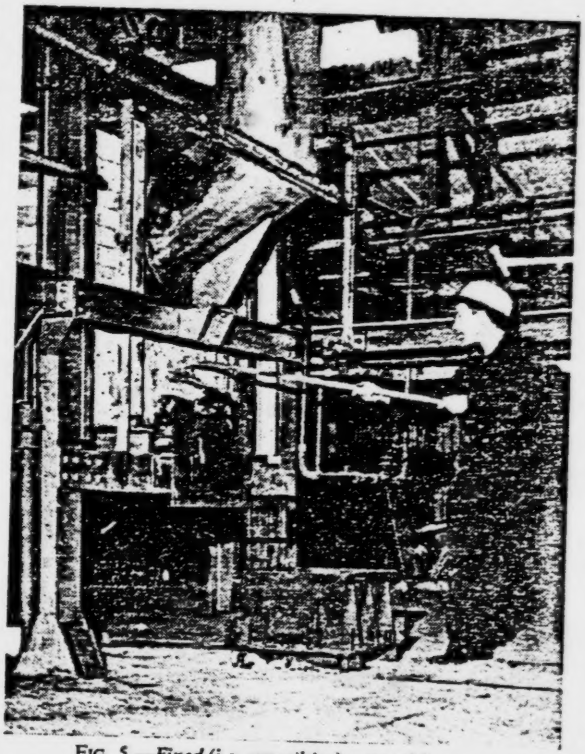

Fig. 5.—*Fixed* (i.e. *non-tilting*) *type of furnace*

The article, in its final shape, is made in a one-stage operation direct from molten material, since adjustment after heat treatment is difficult owing to the extreme hardness of slagceram. Facilities for casting into sand moulds and sectional metal moulds, as well as glass-pressing equipment, are available on the pilot-plant, the choice of shaping method being dependent on the intended application of the product. Material which has been cast into a sectional metal mould or formed by pressing has a smooth surface which is suitable for polishing or enamelling, whereas sand-cast surfaces are rough and coated with a layer of fritted sand. In general, most of the methods used to form glass can be adopted to shape slagceram if they are modified to take account of the different viscosity-temperature relationship.

Heat treatment facilities consist of two small electrically heated furnaces, one larger electrically heated furnace, and one electrically heated kiln which can be operated either as a conventional furnace or a small tunnel kiln. All equipment is controlled automatically and all kiln furniture is fabricated from heat-resisting steel, though more conventional materials, *e.g.* sillimanite, would be used on a larger plant. Figs. 4, 5 and 6 show some of the pilot-plant units.

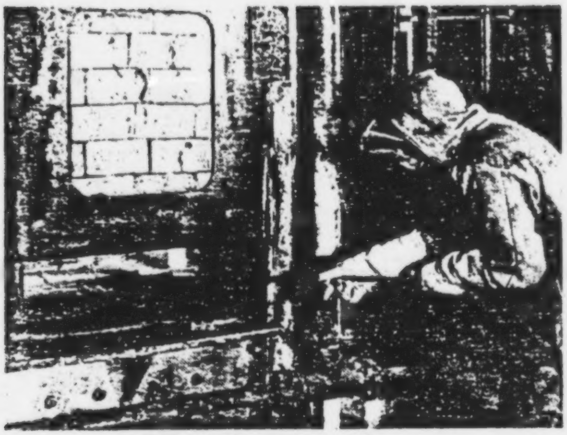

FIG. 6.—*Heat-treatment furnace*

A wide range of products has been made, relatively simple shapes being favoured at this stage. Tiles of various shapes and sizes in plain and polished slagceram, and also the uncrystallised glass, have been a feature of production. The maximum sizes of product which it is possible to make is limited only by the ability of the material to fill the mould, and large, thin sections are possible, given the correct design of mould and feeder system. Typical products include (dimensions in inches):

Floor and Wall Tiles 6 × 6 × ½, 6 × 6 × ¼, 9 × 6 × ½
(plain and patterned) 12 × 12 × ¾, 3 × 3 × ½, 4½ × 4½ × ½
and octagonal tile
Chute linings 8 × 8 × 1¼, 8 × 4 × 1, 9 × 4½ × 3, 8 × 4 × 1,
tapering to ½
Lintels and window sills 42 × 6 × ¾, 42 × 8 × 1
Large panels up to 24 × 24 × 2

Properties of Slagceram from Pilot-Plant

Most of the properties described below were determined on a limited number of samples of pilot-plant products. The properties of the full-scale production material may well be different, but the provisional values listed below are some indication of what may be expected.

The slagceram tested was the solid, *i.e.* not foamed, form. Very few test results are available on foamed slagceram but the following published data on the corresponding Russian product (foamed slag sitalls)[7] may serve as a guide:

Density 150–800 kg./m.^{3}
Modulus of rupture 20–300 kg./cm.^{2}
Water absorption 4·5–9·0%
Impact test 9·7 kg.cm./cm.^{2}
Thermal conductivity 0·11 kcal/(deg. c.m.hr.)
Softening temperature 980–1000°c
Coefficient of linear expansion 7·2× 10^{-6}

Data on the properties of the current pilot-plant product are presented below.

Specific gravity (bulk): 3·00. This is somewhat higher than that of the glass (about 2·90), and reflects the shrinkage, offset to some extent by the development of pores, that accompanies crystallisation.

Specific heat: 0·17 cal/(g. deg. c) at room temperature.

Coefficient of linear expansion: 5 × 10^{-6} per deg. c at room temperature. By analogy with glass ceramics, it may prove possible to change the value of this coefficient to some extent.

Crushing strength: 30,000 lb./in.^{2} for a standard three-inch cube. This value was obtained with cubes of slightly irregular shape, and so is probably low. For comparison, a rapid-hardening Portland cement cube, 28 days old, might have a strength of 8000 lb./in.^{2}

Modulus of rupture has been determined in a simple machine with four-point loading. Considerable difficulty has been encountered in making undamaged test pieces, and the results show wide scatter. A value of about 20,000 lb./in.^{2} seems typical for the pilot-plant material.

Porosity. This was determined by vacuum soaking with water. With one batch, whose porosity was 4·4%, pore sizes were found, from the intrusion of mercury at pressures up to 1800 p.s.i., to fall into two ranges: 0·2–0·3 microns and 50–1000 microns (assuming a contact angle of 140° between mercury and the specimens, and cylindrical pores). Porosity varies to some extent between batches, and values as low as $< 0{\cdot}5\%$ have been observed.

Scratch hardness. 8–9 on Mohs' scale, *i.e.* between that of topaz and of corundum.

Scratch resistance. This was determined by a method similar to that used for paints (DEF 1053, Method 14). A load of 1300g. was applied to the specimen through a pyramidal diamond point while the specimen was drawn beneath the point. A wider scratch indicates poorer resistance, and the mean value of scratch widths for slagceram was about 0·037 mm., less than half those for a glazed tile and a quarry tile.

Abrasion resistance. The machine used for the abrasion test is a multiple version of that described in BS 784:1953. Four specimens, each measuring 6 in. × 4 in. on the face were abraded with washed river sand passing a 14 mesh BS sieve. The specimens were weighed at intervals and the weight losses converted to volume losses, using the densities of the specimens. The abrasion resistance of slagceram was, on this basis about three times that of a good ceramic tile.

In an abrasion test of a type used for refractories, slagceram was found to be about twice as abrasion resistant as cast basalt.

Thermal stability. This was measured according to BS 1902 of 1952. In this test the sample was heated to temperatures up to 900°c, cooled and re-measured. No change in volume could be detected with slagceram. There is some slight evidence that after heating to 1000°c and cooling there is a small increase in volume.

Impact resistance. This was measured by the falling weight test (BS 1811 of 1961) with round-ended weights of 10 lb allowed to fall repeatedly on to the specimen from increasing heights. The behaviour of slagceram was similar to that of ceramic floor tiles, both failing at 2 in.

Coefficient of friction. This was measured by finding the force to start and keep moving a rectangular steel block weighing 3 kg. and about 4 × 2 in. in area over the test surfaces. The values obtained were about 0·5 (limiting) and 0·4 (dynamic) for as-cast slagceram tiles, compared with 0·7 and 0·7 for unpolished new ceramic tiles, and 0·4 and 0·4 for polished worn ceramic tiles. The test panel in a busy part of the floor of the Battersea laboratories (Fig. 7) will be used to obtain the corresponding figures for polished worn slagceram, but on present showing it will be a long time before wear develops.

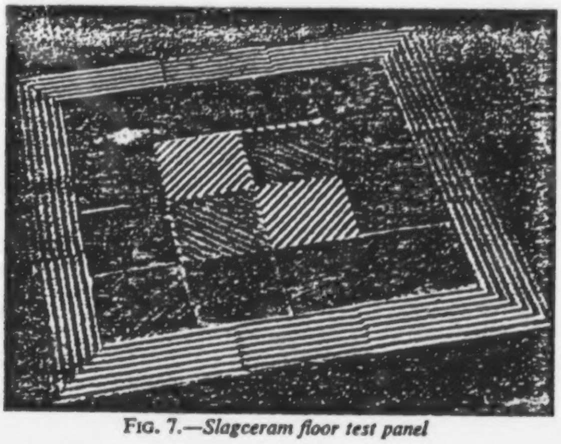

FIG. 7.—*Slagceram floor test panel*

Effects of concentrated loads: no measureable indentation by a ½ in. ball bearing with a load of 500 lb after several weeks. In a short variant of this test, slagceram tiles failed at loads of 2120 lb, 1540 lb and 1370 lb, compared with loads of 930 lb, 1110 lb and 1050 lb for ceramic tiles.

Long-term constant temperature expansions: 0·004–0·006%. This test is on pre-dried tiles at room temperature and 90% relative humidity. The value obtained is negligible, and corresponds to the limit of accuracy of the apparatus.

General floor performance. The test panel at Battersea has shown no noticeable wear, cracking or chipping after almost one year of use.

Exposure test. Tiles at Battersea, London (industrial urban site), show only slight surface discoloration after periods of up to 2½ years. Tiles exposed under Brighton Pier to give immersion for about half the total time have shown no deterioration after five months. At a site near a power station and the sea, salt deposition was pronounced, on cracks, but no deterioration has so far been observed. Tests at Stratford, London, an exceptionally corrosive industrial/urban site, where diesel exhaust fumes are combined with pollution from chemical works, including a sulphuric-acid plant, have so far also given satisfactory results.

The exposure test results have corresponded to those of various accelerated-weathering procedures.

Resistance to mould growth. For this test a number of slagceram tile specimens were sprayed with a spore suspension of the following: (a) *Aspergillus niger* (b) *Paccitomyces varioti*, (c) *Stachybotrys Atra* and (d) *Trichoderma viride*, as specified in BS 1982 of 1953 Part 2. They were maintained at room temperature and 100% relative humidity. After 12 weeks the specimens were examined. They were found to hold scattered mycelia and spore masses on both the broken and moulded surfaces. The masses were very difficult to see and did not impair the appearance of slagceram.

Adhesion. Slagceram can be mounted in ordinary cement, but with smooth slagceram the bond is only moderately strong, even after 28 days' curing. Better results are obtainable with the rougher surfaces. A filled epoxide adhesive gives a very strong bond, failing in the adhesive layer at a tensile load of over 575 lb on a ½ × 2 in. surface.

Volume resistivity. About 8·5 and 7·9 as $\log_{10}$ ohm.cm., these values being found in accordance with BS 2782 of 1957, Method 202A, before and after respectively, "Long Term Damp Heat Ageing" to DEF 5011, 38–42°c, 90–95% relative humidity for four days at room temperature.

This resistivity is low enough to bring slagceram into the category of anti-static flooring materials.

Tracking. A sample was tested for tracking in accordance with BS 3781 of 1964. Slagceram was "no-tracking" at voltage up to 1000 V., the limit for this method. Slight erosion occurred at the maximum voltage.

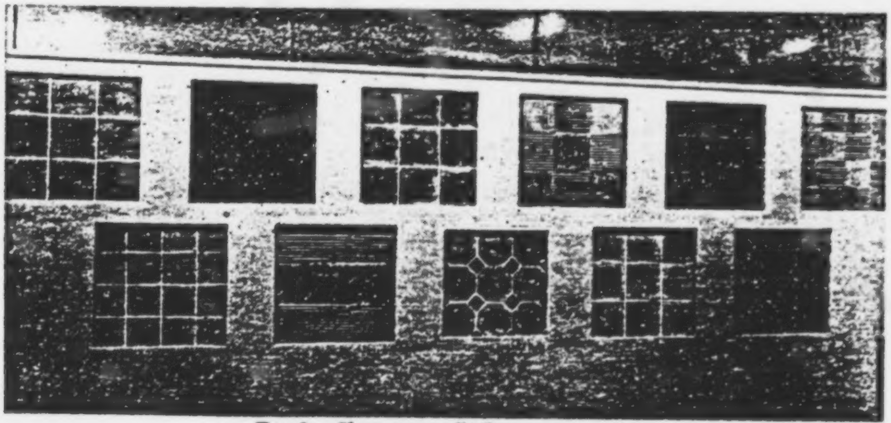

FIG. 8.—*Slagceram wall-tiles arrangements*

Resistance to chemical attack was determined by immersion in the appropriate solution. Some of the results are shown in the Table. It is evident that the slagceram of the present composition is unsuitable for several applications, but even so would have a wide range of uses. With higher silica contents better resistance to acid attack would probably be obtained. In view of the greatly inferior corrosion resistance of a slagceram glass compared with that of the corresponding slagceram, it is likely that the amount of residual glass in the slagceram would have a considerable influence.

Colour and general appearance. The present pilot-plant products are generally an attractive black or grey, and the corresponding glass jet-black. By using different compositions and process conditions other colours can be obtained, *e.g.* an almost white slagceram, an almost colourless glass, and red-brown and greenish slagcerams have been produced in the laboratory. Attractive combination of different tile finishes are possible (Fig. 8).

Uses of Slagceram at Present

A number of test panels have been on site trial for several months with encouraging results. These panels provide examples of the present uses of slagceram.

Wear-resistant chute lining

Test panels are being evaluated under arduous conditions in chutes handling sintered iron ore and metallurgical coke. The conventional lining for such a chute is basalt. After many months' usage, slagceram is showing no sign of wear.

As a floor material

(i) *Normal wear due to pedestrian traffic*

No wear or chipping has been noted after several months' wear on a slagceram-tile floor panel in a busy laboratory and office passage and the appearance of the flooring improves with time.

(ii) *Wear due to industrial traffic*

A panel of 9 in. × 6 in. × ½ in. tiles was placed in a position of heavy wear during a plant overhaul. Heavy equipment was pushed and dragged over the

Table

Corrosion Tests on Slagceram (exposure time six months)

Corrosive Liquid	*Liquid change visible*	*Surface changes*	*Interior changes*	*Other observations*
10% H_2SO_4	White deposit on bottom of bottle	Soft white coating (0·5 mm. thick). Crystal growth	No apparent middle layer	—
50% H_2SO_4	No change. White deposit on bottom of bottle	White coating beginning to form	—	—
Conc. H_2SO_4	Slightly discoloured	Lightening in colour	—	—
10% HCl	—	Hard white coating 0·5–1·0 mm. thick	Faint mauve layer between coating and grey centre	—
Conc. HCl	Dark yellow deposit on bottom of vessel	Grey hard coating total action penetrated 1·5 mm.	A faint white layer adjoined the outside. A thick mauve layer adjoined the grey-centre	Grey slagceram had diminished quite a deal in size. Surrounded by three layers in all
Conc. HNO_3	—	Hard grey coating 0·5 mm. thick	—	—
10% HNO_3	—	Fairly hard white coating Thin	Mauve middle layer 1·0 mm. thick	Approx. 1·0 mm. thick, three-layer coating
10% CH_3COOH	—	Surface light grey. Minutely thin layer	—	—
Conc. CH_3COOH	—	Surface lighter in colour	—	—
Aqua Regia	—	Light green coating. Fairly hard	White and mauve layers under surfaces	Approx. 1–1·5 mm. thick, three-layered coating
5% NaOH	—	Surface lighter in colour	—	—
Conc. NaOH	—	Brown patches on cast surfaces. Green (faint) tint on cut surfaces. All surfaces lighter	—	—
5% NH_4OH	—	No apparent change	—	—
20% $MgSO_4$	—	No apparent change	—	—
10% Na_2CO_3	—	No apparent change	—	—
Distilled water	—	No apparent change	—	—
Tap water	—	No apparent change	—	—

area for several weeks without any deterioration of the panel.

(iii) *Wear in excessively arduous conditions*

An area immediately in front of a small tank furnace used for melting slag was tiled with 6 in. × 6 in. × ½ in. slagceram tiles. This area is subjected to constant wear from metal trolleys and frequent spillage of molten slag. The average temperature of the floor is about 90°c. Previous floor coverings (concrete and ceramic tiles) had failed within hours, the surface becoming pitted and uneven. After several weeks' exposure only slight surface spalling was noted on the slagceram tiles with no other signs of deterioration.

Many possible uses have been mentioned, and may be envisaged, for slagceram, including the following: kerbstones, paving flags, floor tiles, roof tiles and slates, guttering, drain pipes, stair treads, curtain walling, fence posts, window sills, lintels, tunnel lining, sea defences (*e.g.* breakwaters), dams, building blocks, wall panels, non-skid road surfaces.

It is likely that slagceram properties would match up to those required in the above examples. This would mean that costs would be the major factor governing application. On this, all that can be said at present is that slagceram could well be competitive in the applications enumerated.

In addition to all-slagceram articles, one may envisage composites, such as steel-reinforced slagceram, or slagceram-clad steel (*e.g.* for fire resistance). For fire resistance, the foamed material with its good insulation, would be best. Foamed/non-foamed slagceram "sandwiches" have been produced on the pilot-plant and could have many uses in which high strength combined with good heat (and, perhaps, sound) insulation is needed.

Recapitulation and Conclusions

This paper has sought to show how a search for better uses for metallurgical slags has eventually led to the superior material slagceram. In the development of this material, fundamental scientific knowledge, information from related technologies and extensive experimentation of both systematic and *ad hoc* character have been combined to bring production to the pilot-plant scale and to enable a large-scale production process to be envisaged. Testing of slagceram produced on the pilot-plant has confirmed its interesting properties, and further improvements may be expected as knowledge increases. It is concluded that slagceram has many uses as a road and building material, and it is hoped that this paper will lead to further ideas and, perhaps, to a more realistic list of uses in the light of which potential manufacturers of slagceram could proceed more effectively.

References

[1] Kitaigorodskii, I. & Bondarev, K., Ekonomicheskaya Gazeta, 1961, No. 12, October 23, 31

[2] McMillan, P. W., "Glass-Ceramics," *London and New York: Academic Press*, 1964

[3] "Structural transformations in Glasses at High Temperatures." Edited by N. A. Toropov & E. A. Porai-Koshits, *New York: Consultants Bureau*, 1965

[4] Filipovich, V. N., *ibid.*, p 33

[5] Fefer, A. S., "Method of Obtaining Shaped Foamed Glass-Slag Articles from Blast Furnace Slag Melts." Pp 385–402 of "Metallurgicheskie shlaki i primenenie ikh v stroitel stve," 1962, Gos Izd. lit. po stroitel 'stvu i arkhiterkture

[6] Kitaigorodskii, I., Russian Pat. 787042/29–14, Class 32a, 1702, 1964

[7] "Foamed Slag Sitall" (Penoshlakositall), Donetskii Sovnarkhoz Ukr. SSR, 1963

ASPHALT AND COATED MACADAM ASSOCIATION

A new body, the Asphalt and Coated Macadam Association, has been formed to represent a major section of Britain's road making industry. It will represent the flexible road industry to Government departments and to all other organisations concerned with the promotion and development of roads in Great Britain.

For some years past, the Asphalt Roads Association, the Federation of Coated Macadam Industries, the Road Bitumen Association and the British Road Tar Association have collaborated through the Flexible Road Group in promoting flexible road materials, and particularly in making the public aware of the many advantages obtained from roads constructed with bituminous materials.

It has been decided that this work shall be extended and developed through the new Association, which now replaces the Flexible Road Group. A.C.M.A. will foster the general development of suitable materials and methods of construction.

Mr N. Bourne, who has been elected the first chairman, has said that the formation of this body was an important step forward in representing effectively the interests of the "black top" road makers, and would strengthen the services given to highway engineers by this section of the industry which has been responsible for 90% of the surfacing of Britain's roads and 80% of our motorways. He added that the industry was constantly developing new methods and techniques in order further to improve productivity and the new Association would be actively engaged in stimulating this work.

The offices of the Association are at 14 Howick Place, London, S.W.1. The officers of A.C.M.A. are: Mr W. Mervyn Law (director), Mr L. G. Watkins (consultant), Mr M. F. Adcock (secretary).

Reference 7

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Bibliography

1. E. Duer Reeves, "Industrial Research—A Kind of Business Strategy," *Chem. Eng. News* **43** (43), 92–98 (Oct. 25, 1965).
E. Duer Reeves, "Industrial Research as a Corporate Function," *Workshop Syllabus on Management of Industrial Research*, Sect. I, Industrial Research Institute, Inc., New York, 1968.
2. R. Landau and B. Brown, "Making Research Pay (Management Oriented Topics)," *Inst. Chem. Engrs. Symp. Ser.* **1965**, (7) 7.
3. "Productivity in Research," *Inst. Chem. Engrs. Symp. Ser.* **1963**, (13).
4. P. Docksey, *The Objectives of Industrial Research*, in reference 3.
5. R. L. Merrill, *The Wall Street Transcript* **15** (5) (Jan. 30, 1967).
6. F. C. Croxton, *New Techniques for Increased Research Productivity*, in reference 3, p. 8.
6a. S. Lenher, "Organization and Management of Science," *Res. Management* **12** (6), 425–436 (1969).
7. *Chem. Eng. News* **45** (33), 15 (Aug. 7, 1967).
7a. C. A. Stokes, *Res. Management* **9** (6), 339–349 (1966).
8. *Am. Inst. Chem. Engrs. Symp., St. Louis, Mo., Febr. 18–21, 1968.*
8a. L. A. Wilkinson, *Project Management—Getting the Job Done*, in reference 8.
9. L. Adler, "Systems Approach to Marketing," *Harvard Business Rev.* **1967** (May–June), 112.
10. E. S. Quade, ed., *Analysis for Military Decisions*, The Rand Corp., Santa Monica, Calif., 1964, p. 4.
11. W. S. Fedor, "Management by Systems," *Chem. Eng. News* **45** (36), 123–124 (Aug 28, 1967).
12. E. C. Hughes, "One Key to R & D Success: The Right Kind of Proposal," *Res. Management* **12** (1), 43–55 (1969).
13. M. R. Cine et al., "Pilot Plant Development of a Polyethylene Process," *Chem. Eng. Progr.* **54** (2), 245–254 (1961).
14. K. C. Buell, "The Development of Marlex," *Res. Management* **4** (4) 245–254 (1961).
15. D. S. Hall and J. W. Davison, *Process Development of Cis-4 Polybutadiene*, in reference 8.

C. A. Stokes
Consultant

S

SLAGCERAM

Slagceram is a material of the glass-ceramic type, produced by the fine and uniform crystallization of glass made from metallurgical slag. Slagceram was developed by the British Iron & Steel Industry Research Association (BISRA), with the aim of making slag, a major steel-industry by-product, more profitable by upgrading it into a higher-value market, and of doing so on a scale that would deal with a significant proportion of the slag output (reckoned in millions of tonnes, t) (1,2). So far, the large-scale aspects have not been realized, and the material is in commercial production only on a small scale. The smallness of the scale of production means that production costs are high, and the market is restricted to special wear-resisting shapes. Materials similar to slagceram have been reported from the U.S.S.R. (3) and Japan (4) but the scale of production is not known.

Slags and Their Utilization

Pyrometallurgical operations generally yield two molten materials: metal (or a metal-rich phase) and slag. The slag contains most of the nongasifiable impurities from the metal-bearing feed and the fuel, plus the nongasifiable part of the fluxes added mainly to obtain metal of the required purity. The metal is the main product, and it is therefore sound economic sense to make its quality and rate of production the main factor, hence the slag properties which influence its utilization are subordinate, and any changes usually have to be made after the slag has left the main metallurgical process. A wide variety of slag-utilization technologies have been developed to cope with this situation, and a review of those used for steel-mill slags has been published (5).

Though it can be made from various slags, slagceram is mainly associated with those from the iron blast furnace. This plant produces anything from about 0.25 to about 1.2 t of slag for every tonne of metal. The amount depends mainly on the purity of the iron-ore feed, the composition of its impurities, and the ash and sulfur content of the coke fuel. These factors not only have a direct effect, but also an indirect one because they govern the amount of flux (in almost all cases a lime- or magnesia-rich material) that has to be charged into the furnace to ensure that metal purity is right and that the production rate is not restricted by the viscosity of the slag at the temperatures prevailing in the critical parts of the furnace. These requirements and the growing tendency to import purer materials from large mining undertakings mean in practice that iron blast-furnace slags are rather similar in composition wherever they are produced (Table 1).

The relationship of slags to minerals in the $CaO\text{-}SiO_2\text{-}Al_2O_3$ system and certain other technologically important materials is shown on the liquidus diagram (Fig. 1) at 5% MgO. For U.K. slags the melilite is mainly a gehlenite–akermanite solid solution; many other phases are found, not all of which appear in Figure 1.

Table 1. Chemical Composition of Iron Blast-Furnace Slags from Different Parts of the World

Location	Composition, wt %						
	CaO	SiO_2	Al_2O_3	MgO	FeO	MnO	S
U.S.A., Great Lakes	40.2	38.5	7.9	11.3	not known	0.3	0.9
U.S.S.R., Siberia	39.3	37.4	12.5	5.6	0.5	0.4	0.6
Japan, Honshu	41	34	14.7	5.8	not known	0.7	0.8
U.K., Teesside	37.9	31.3	17.9	6.8	0.6	0.9	1.9

In addition to the components shown in Table 1, iron blast-furnace slags sometimes contain alkali-metal oxides, derived mainly from coke, up to a maximum of a few percent.

Blast-furnace slags are occasionally (because of local economics or managerial decisions) treated as wastes and dumped; and, in very unusual circumstances they have been treated as a coproduct with iron in the sense that the attainment of the composition needed for a particular slag use has dictated furnace operation. For the most

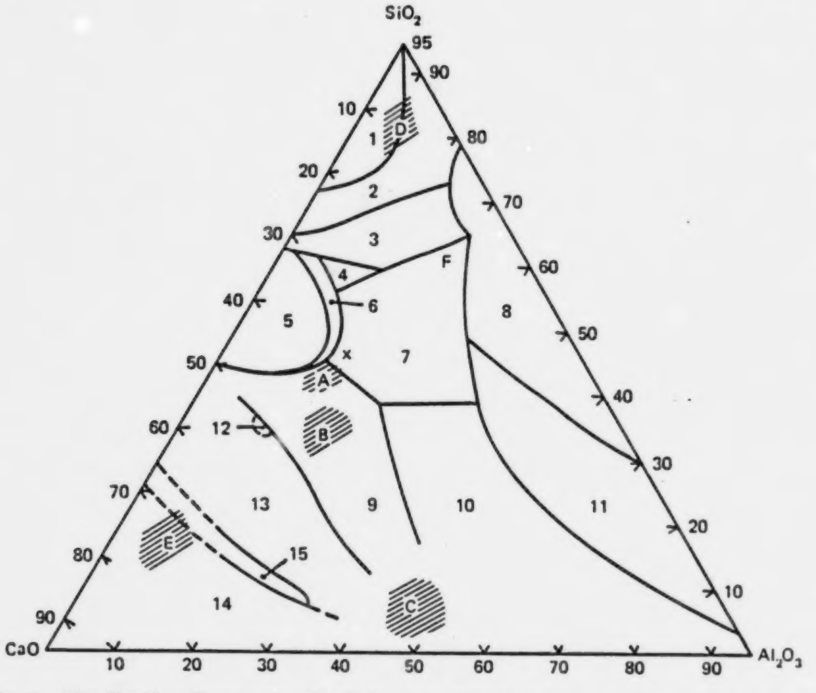

Fig. 1. The liquidus diagram for the $CaO–Al_2O_3–SiO_2–MgO$ system at 5 wt % MgO. Main fields shown by numbers: (1) two liquids; (2) cristobalite, SiO_2; (3) tridymite, SiO_2; (4) clinopyroxene, ca $CaMgSi_2O_6$; (5) pseudowollastonite, $CaSiO_3$; (6) wollastonite, $CaSiO_3$; (7) anorthite, $CaAl_2Si_2O_8$; (8) mullite, ca $Al_6Si_2O_{13}$; (9) melilite, $Ca_2MgSi_2O_7$(acermanite)–$Ca_2Al_2SiO_7$(gehlenite); (10) spinel, $MgAl_2O_4$; (11) corundum, Al_2O_3; (12) merwinite, $Ca_3MgSi_2O_8$; (13) dicalcium silicate, Ca_2SiO_4; (14) lime, CaO; (15) tricalcium silicate, Ca_3SiO_5. Position of typical slagceram shown by X; ranges (not necessarily at 5 wt% MgO) of other technologically important materials shown shaded: (A) acid blast-furnace slag; (B) ordinary (U.K.) blast-furnace slag; (C) high-alumina cement; (D) commercial glass; (E) Portland-cement clinker; and (F) copper slag.

part, however, slags are considered a by-product that the furnace operators are happy to see the last of, at a price sufficient to cover the slag-handling costs in the steelworks and with no interference with furnace operation.

Slags from the iron blast furnace already have many uses. For example, if allowed to cool in air they crystallize and can be crushed to form an aggregate suitable for use in concrete, as a roadstone, a filter medium, or a feed component in glass or Portland-cement making. Slags treated with water–air–steam mixtures form a pumice-like material for use in light-weight concrete. They can be cast into shapes, such as paving blocks, which crystallize during the annealing and slow cooling needed to prevent cracking. Finally, if a stream of molten slag is treated with a large excess of water the cooling is so rapid that a mainly glassy material is formed, which has the useful property of being easily transformed into a cement by fine grinding and addition of lime. All this can be done without changing the composition of normal iron blast-furnace slags.

With suitable composition adjustments, blast-furnace slag can be transformed into a glass so stable that it does not crystallize even with the slow cooling needed with large masses to prevent cracking, or during several hours' annealing. This is one way of raising the value of blast-furnace slags and has been used to produce glass articles of attractive, generally jet-black appearance, but rather poor mechanical properties (Mohs hardness 4½–5½, rupture strength 39.2 MN/m^2) and chemical resistance (rapid formation of colloidal deposit when immersed in acid) (1).

Production of a stable glass from slag is of more interest as a step on the way to slagceram. What is needed here is virtually complete crystallization of the glass to form fine (of the order of 1–20 μm) crystals of reasonably uniform size. It is on these features that the specially desirable properties of slagceram depend. Fine and uniform crystallization is not achieved with ordinary slag or ordinary slag glass. This is mainly because in materials of such compositions crystallization proceeds from the surface or from gross discontinuities in the glassy material, ie, from crystallization centers that are relatively scarce and unevenly distributed. The essence of slagceram technology is that the slag glass has a composition that generates large numbers of crystallization centers (or nuclei) uniformly in any given region of the glass before appreciable crystal growth starts on them. This separation in time is achieved by making the two processes (nucleation and crystallization) occur at different temperatures and imposing a suitable schedule of temperature variation with time. The theory behind these processes is outlined in the next section.

Principles of Slagceram Formation

Nucleation and Crystallization. The theory of nucleation and crystallization has, along with other scientific aspects of slagceram, been treated in considerable depth by Davies et al., whose paper also provides a good bibliography (2). Only an outline will be given here.

As in any supercooled liquid, random fluctuations in slag glass continually give rise to more-ordered regions, ie, potential nuclei. The special glasses from which slagceram is made are designed to generate high concentrations of nuclei at a temperature (which turns out to be close to the annealing temperature) so low that the mobility of atoms and atomic groupings in the glass is insufficient to allow the considerable rearrangements that accompany crystal growth to take place at significant rates. When the temperature is raised the mobility increases and crystals grow on the nuclei. The nucleation and crystallization processes have their own temperature ranges in which the rate rises to a maximum and then falls off. It should be noted that in nucleation the rate is measured as the number of nuclei produced per unit volume of the glass in unit time, while in crystallization it is the rate of crystal growth. The ranges overlap, but for slagceram-type crystallization to occur the maxima must be well separated in temperature.

In a supercooled (ie, metastable) glass, the separation of more-ordered regions, which can be regarded as a step on the way to the stable crystalline state, would be expected to be accompanied by a decrease in the free energy of the system. The decrease is proportional to the volume of the region, or, for a spherical region, to the cube of its radius. On the other hand, the separation of the region will produce a new surface, accompanied by a free-energy increase proportional to the surface of the region, or, for a spherical region, to the square of its radius. The netfree-energy change of the system due to the separation of the region will thus be the sum of two terms, a negative one proportional to the cube of the radius and a positive one proportional to the square. In accordance with the normal behavior of functions of this type the effect of an increase in the radius from zero will be first to increase the free-energy change (ie, the free energy) of the system to a maximum and then to reduce it. In other words, only those regions whose radii exceed that corresponding to this maximum (the critical radius) will have a tendency to grow, ie, they are nuclei. The smaller, transient regions are known as embryos. In this discussion the embryos and nuclei have been assumed to be spherical. This is reasonable because a sphere has the lowest surface–volume ratio, ie, the lowest contribution to the positive surface-dependent free-energy-change term. The general considerations would, in any case, apply to regions of other shape.

Nucleation of the type considered is called homogeneous, ie, it occurs in a homogeneous phase. There may, however, be discontinuities already present in the phase. Such discontinuities (themselves formed by a homogeneous nucleation and crystallization process) will, if their atomic arrangement is suitably related to that of the nucleating material, facilitate formation of the nuclei.

Theoretical treatment of nucleation leads to an equation giving nucleation rate as a function of temperature in which the free-energy-change maximum, corresponding to the critical radius, occurs together with the activation free energy for the assimilation of atoms or molecules across the interface of the new phase. Each of the free-energy changes is in an exponential term, the net result being that with increasing temperature the rate rises to a maximum and then falls away.

In addition to the nucleation mechanisms considered above, the new phase may separate spontaneously by spinodal decomposition, leading to glass-in-glass separation. It can occur when the normal spontaneous local fluctuations in composition result in a decrease in the free energy of the system, which is the case, eg, if a foreign network-forming ion present in the glass causes sufficient distortion of the main silicon–oxygen–silicon bonds.

To turn now to the question of the rate of growth of crystals on the nuclei. The main factor here is the rate at which the slowest-moving component involved in crystal growth moves. This factor is related to the viscosity and temperature in such a way that, as with nucleation, the crystal-growth rate increases with rising temperature to a maximum and then falls away. As already noted, slagceram formation depends on adequate separation in temperature between the nucleation and crystallization rate maxima.

Transformation of Molten Glass into Slagceram Articles. The overall transformation of the molten slagceram glass into the finished slagceram object, involving homogenization, shaping, nucleation, and crystallization, can now be discussed in terms of the nucleation and crystal-growth processes just considered. The transformation is illustrated in Figure 2, which shows how the temperature, content of glass, number of nuclei, and size of crystals (all in arbitrary units) change with time.

Before A, the batch of slag and additives (discussed later) in the right proportions have been brought into the fully molten condition. From time A to B the composition of the molten glass is being made homogeneous, an operation that, with viscous glasses, can take a long time in the absence of stirring. From time B to C, the temperature of the glass is being adjusted to that required for shaping (this temperature will depend on composition, shaping method, and shape). The shaping operation is carried out at C, and the shaped article is then cooled to the nucleation temperature range, which is reached at D. An alternative temperature schedule between C and D would be to cool the shaped article to room temperature and reheat it later to the nucleation temperature range; but such a schedule involves more danger of cracking, as well as increased process time, and would only be used in special circumstances. Nucleation starts at D and gathers speed as the temperature approaches that for the maximum rate (reached at time E). Nucleation dies away by time H, but before this has been reached crystals have started to grow (at time G) on the nuclei. Before G the material appears virtually completely glassy; after G the nuclei become increasingly enclosed in crystals. Between times F and I, the temperature is being raised to that (reached at time I) giving the maximum crystal-growth rate. At time J, when very little glassy material remains, the final cooling of the article starts; it can be carried out faster than would be possible with the corresponding uncrystallized article.

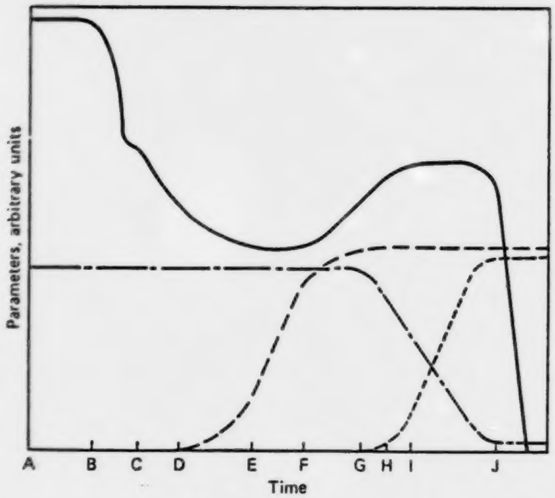

Fig. 2. Variation of temperature and other parameters during slagceram production. LEGEND: temperature ———; proportion of material in glassy state —-—-—; number of nuclei — — — —; size of crystals -----.

Alteration of Slag Composition and Effects of Melting Conditions. The changes needed in chemical composition to make slagceram from iron blast-furnace slags will now be discussed. A general point is that, because the slag is usually the cheapest of the components and because the making of any addition involves processing costs, the change is made as small as possible. The composition change to convert the slag into a stable glass can be implemented by adding silica and/or alumina, ie, materials that are network formers (in the glass sense). Silica is cheaper and (possibly in combination with minor additives) generally gives a glass of better liquidus temperature for melting and assimilating additives, and better viscosity temperature-dependence for shaping by some of the methods established for ordinary glasses. Silica addition also alters the nature of the minerals, favoring those that make the mechanical and chemical-resistance properties of slagceram better than those of slag. Finally, silica addition increases the viscosity of the glass sufficiently to prevent the uncontrolled nucleation and crystallization characteristic of slag. The slagceram composition to which most attention has been given is that obtained by adding about 30 parts by weight of silica sand to 100 of the "U.K., Teesside" slag listed in Table 1.

In addition to the change in the content of the main components, the transformation of slag glass into slagceram requires the presence of a few percent of minor components to produce nuclei at the right stage. These nucleating agents can be any one, or various combinations of, a wide variety of materials. They include transition-metal oxides and sulfides, which, since they are already present to some extent in the slag, are of special interest for slagceram. The nucleating agents studied in greatest detail for slagceram are a combination of chrome ore (about 47% Cr_2O_3) with titania, and various forms of iron oxide. Because iron oxide is cheap, present in slag, and plentiful in steelworks, this is the preferred nucleating agent. Like many other nucleating agents, the above are sensitive to the state of oxidation of the glass, being most effective under reducing conditions. For this reason, additions of coke are often beneficial, and the conditions under which the glass was melted can have a decisive effect on the extent and type of crystallization in the final product. For example, for slagceram nucleated with iron oxide the melting conditions can, with the same nucleation and crystallization schedule, give slagceram of two distinct types or a glass that fails to crystallize properly, probably because it does not have enough nuclei. The general effect is that with short times in the molten state a dark, fully-crystallized slagceram is obtained; as the time molten is lengthened the glass shows an increasing tendency to give an incompletely crystallized or even uncrystallized product; with still longer times molten (on a laboratory scale), a slagceram relatively light in color begins to appear; and with even longer times there is again a tendency for crystallization to be incomplete or absent. It is both scientifically and technologically interesting that addition of carbon to the melt enables the time molten with which slagcerams can be obtained to be extended on both laboratory and larger production units. In fact, melts held in the furnace so long that the glass shows no tendency to form slagceram can be restored by coke addition, and the over-cooking–restoration cycle can be repeated.

The mineral phases present in the dark- and light-colored slagceram are the same: clinopyroxene is the main component with, sometimes, small amounts of melilite. However, in the dark material the crystallization takes the form of spherulites, in the light it is mainly dendritic. The nucleation in the dark material is probably heterogeneous, and homogeneous in the light. The effect of the time the glass is held molten is most probably due to the influence it has on the state of oxidation under the normally oxidizing furnace atmosphere necessary for high fuel efficiency. The influence of changes in furnace atmosphere does not make itself felt quickly, because the high viscosity of the slag glasses retards mass-transfer. An example of this is that when the slag is taken in the liquid state direct from the highly reducing conditions of the blast furnace rather than as a solid made by crushing air-cooled slag, a very oxidizing atmosphere in the melting furnace (where the sand and nucleating agent are added) can be maintained without loss of effectiveness of nucleating agents.

The melting conditions, through their effect on nucleation, also influence another important technological factor, the ability of the shaped slagceram-glass object to maintain its shape during the nucleating and crystallizing heat treatment without mechanical support. With the right conditions, the loss of shape (slumping) is negligible, probably because a skeleton of crystallized material, with a softening temperature greatly exceeding that of the glass, is produced while some of the glass is still strong enough to resist the forces due to its own weight and surface tension.

Although a single slag composition was used for the bulk of the slagceram development work, it has also been established that other iron blast-furnace slags and slags of completely different type could be used. It is usually possible to predict what modification to the process would then be required. The slag compositions studied include at least the following approximate ranges: $CaO:SiO_2$ ratio 0.9–1.4; 15–21% Al_2O_3; 5–35% MgO; 0.6–1.1% FeO; 0.4–1.1% MnO; 1–1.8% S. With various nucleating agents, degrees of oxidation, and other factors, a considerable range of slagceram colors can be obtained, eg, orange, brown, or off-white.

Slagceram Production

Pilot Plant. The original development work on slagceram was done on melts up to about 9 kg in mass. The melts were produced from solid components in indirectly heated salamander crucibles, which, by maintaining reducing conditions, facilitated the subsequent crystallization of the glass. Conditions were in fact so reducing that there was some loss of iron oxide nucleating agent through its reduction to metallic iron.

Production on a pilot-plant scale was first aimed at producing slagceram in quantities sufficient for the reliable evaluation of its properties; later stages of the work were aimed at developing at least one technology for the commercial production of slagceram on a small scale and at getting pointers to the best technology for large-scale commercial production. The feed for the bulk of the pilot-scale work consisted of 13–19-mm pieces of cold slag (the U.K. Teesside slag of Table 1), ordinary builders' sand, and 50–15-μm nucleating agent. The mass ratio of slag to sand in most batches was 100:30, but special batches of higher sand content were occasionally made to study the effect of higher silica content on the production technology and properties of slagceram. The batch usually contained a few percent of nucleating agent, coke sometimes also being added at the rate of about 10% of the batch mass to maintain the relatively beneficial reducing conditions in the melt with oxidizing atmospheres in the direct-fired furnaces.

In the main pilot-plant work two procedures were used for melting the batch. In one, it was first charged into a cylindrical rotary furnace closed at one end (a design based on the Kaldo steel-making unit) and fired with an oxy-propane burner. The rotation of the furnace greatly accelerated the melting of the solids and homogenization of the melt. Although a brief treatment in the rotating furnace was sometimes all that was needed for a satisfactory slagceram glass to be produced, the melt was usually transferred into a glass-tank type of furnace for a further period of homogenization and general conditioning. The degree of homogeneity needed for an opaque, crystalline material such as slagceram is, of course, considerably less than for a clear glass. Nevertheless, care had to be taken that no significant numbers of solid particles remained, since these would have produced uncontrolled, coarse crystallization, and that variations in the composition of the liquid should not be sufficient to lead to regions of different crystallization characteristics in the final articles, since they might then have cracked or distorted during the crystallization heat treatment. In the second procedure the batch was charged directly into the tank (ie, nonrotary) furnace.

The mass of a batch melted varied from 0.1 to 1 t. One of the factors was that, because the slagceram glass was dark and viscous it was difficult with normal top heating to get a uniform temperature down a deep bath without stirring (this difficulty arises in the glass industry, but not with clear, colorless glasses). The bath depth in the tank furnaces was therefore normally limited to 75–100 mm, which is considerably less than in normal glass tank furnaces. A greater bath depth with slagceram glass could be used in another pilot-plant furnace, operated by the Steetley Organization Research Department, Worksop, U.K., which was of the continuous type and had bottom as well as top heating. Coke was found to be unnecessary with this furnace, probably because of the greater bath depth and consequently relatively smaller surface exposed to the furnace atmosphere.

In addition to the above procedures, based on cold slag, tests were carried out with molten slag direct from the blast furnace. Such a technology would have many advantages for large-scale slagceram production. The molten slag was taken from the furnace in a special insulated pot and poured into one of the rotary furnaces held upright. No special difficulties arose in making the sand and nucleating-agent additions to the molten slag and good slagceram was obtained despite the normal variations in the composition of slag leaving the blast furnace.

The techniques used on the pilot-plant scale for shaping the slagceram glass included pressing, rolling, and casting. These are used in ordinary glass making, but had to be modified to take into account the steeper variation of viscosity with temperature of slagceram glass (ie, its shortness) and its low thermal conductivity and dark color. Rolling gives plate of good surface finish and flatness, but special attention is needed in the heat-treatment stage if flatness is to be preserved. Pressing can be used for fairly complicated surface contours on articles of simple basic shape. Casting in sectional metal molds is suitable for somewhat more complicated shapes, while for very complicated shapes, or for shapes needing rough surfaces, sand molds are best.

For the next stage of heat-treating the shaped articles to give nucleation and crystallization, the pilot plant had equipment of various types: batch gas-fired and electrically heated furnaces, and a continuous electrically heated kiln. Because of the sensitivity of the process to temperature, the uniform maintenance of the correct temperature or temperature distribution was a main design requirement. Furnace atmosphere influences the surface finish to some extent, and electric furnaces or muffle-type gas furnaces, which give a greater degree of control, would be preferable where this is an important factor.

The material nucleated with iron oxide was relatively free from distortion of the slumping or twisting type, and was treated by a simpler schedule in which nucleation was obtained without specific nucleation treatment and the rate at which the temperature was raised to the crystallization range was less critical; furthermore the crystallization temperature could be varied over a wider range and the crystallization time reduced. Since the heat-treatment stage is one of the major cost items in the overall conversion of slag to slagceram, this was an important consideration and led to the choice of iron oxide as the nucleating agent in the commercial process.

Variations in composition and heat-treatment schedule enabled a wide range of slagceram crystal sizes to be obtained. The crystal size was an important factor in deciding whether a given article distorted during heat treatment, and had a great influence on the mechanical and chemical properties of the final product.

Commercial Production of Slagceram. Slagceram is produced by C.B.P. Engineering & Construction Limited, Blackburn, Lancashire, U.K. under the registered name of Basramite. The company became interested in slagceram because one of its activities is the design, fabrication, and installation of plant components for service under highly abrasive conditions. This is a small though expanding market, and, from the slagceram point of view, still represents only a small extension of the pilot-plant scale of production. The present facilities are in fact modeled on the BISRA pilot plant, and have a melting potential of about 1 t/day.

The melting furnace is direct fired, with a bath about 1400 mm long and 760 mm wide. The design provides for operation with a bath about 13 mm deep, ie, a total charge of about ½ t, the minimum charge for a bath of adequate depth being about 300 kg. The charge is cold, crushed slag, sand, and nucleating agent. The furnace is fired with five gas–air burners directed across the top of the charge, the time to melt and homogenize a 300 kg charge being about 4.5 hr. No heat recuperation is provided, and the fuel consumption is therefore high. The temperature of the homogeneous melt is checked with an immersion thermocouple, and if it is correct for the particular shape and shaping procedure, the furnace is tilted to run the melt through the tapping hole into a lined intermediate ladle, from which it is poured by hand into the shaping facility. To prevent distortion, the more complicated shapes are left in molds during heat treatment, which adds considerably to costs. Sectional metal molds are used for flat shapes and CO_2-hardened sand–silicate molds for more complicated shapes.

The heat treatment, involving nucleation at about 700 and crystallization at about 900°C, is carried out in a gas–air-fired furnace 900 × 1200 × 1200 mm in internal dimensions. The crystallized articles are removed from the furnace at about 400°C and packed in vermiculite for the rest of the cooling period.

Basramite linings have been installed, and given service at least as good as cast basalt, in various plants: for example, in cyclones for the dirt-extraction system in a paper pulp line or for a line conveying nonpulverized ash in a boiler-firing system. Basramite has also been used as part of a venturi in a pulverized-fuel ash disposal system, and as an elbow lid for a pulverized-fuel burner at a power station.

While in many applications Basramite is a replacement for cast basalt, it is sometimes used for shapes that cannot be made in that material. As experience is gained, and the advantages of wear-resisting linings in general become better known, the market for Basramite will increase. However, it is not likely that the wear-resisting-linings market will ever rise enough to enable production costs to be reduced to what could be expected from, eg, a plant making slagceram tiles at the rate of 300 t/day.

Large-Scale Production of Slagceram. Production of slagceram on a scale large enough to bring the price into the mass-market range could be carried out in various ways. The choice would depend on the type of product and on whether the works were located near enough to the metallurgical plant for the process to be based on liquid slag.

A likely flowsheet is shown in Fig. 3. In view of the advantages of the higher production rates and lower fuel consumptions obtainable when slag is charged into the melting furnace in the liquid state, it is likely that slag will arrive molten in ladles, which will then be tipped either into a holding vessel or directly into the furnace. With a furnace of the continuous glass-tank type, slag flow from the holding vessel or ladle would be automatically controlled to give a steady flow into the furnace, the solids being dispensed by continuous weigh feeders from their bunkers. Alternatively, the tank furnace could be preceded by two or more relatively small rotating furnaces in which batches of liquid slag and the solid components would be quickly converted to a somewhat heterogeneous liquid for final homogenizing and conditioning in the tank furnace. In this alternative, batch-proportioning feed systems would be used, and the capacity of the rotary furnaces would be suitably related to that of the slag ladles. In addition to the main feed materials the melting furnace would also receive the reject material from all the stages of the production flowsheet in the absence of other uses (for which, eg, defective slagceram-glass articles could be crushed and the product heat-treated to produce slagceram aggregate). Some subdivision of the melting furnace to provide a final zone for adjusting the temperature of the molten slagceram glass to the best level for the shaping operation might be advisable. The molten glass would then be dispensed via feeders to the shaping plant. This plant would resemble a mechanized foundry if relatively complicated shapes were aimed at; pressing and rolling would be used for simpler shapes and flat products. For slagceram-aggregate production the shaping plant might consist of a granulating unit, or a foaming plant if a light-weight product were desired.

Heat treatment of the shaped articles could be carried out in a continuous kiln with suitable temperatures in different zones. For articles of specially precise dimen-

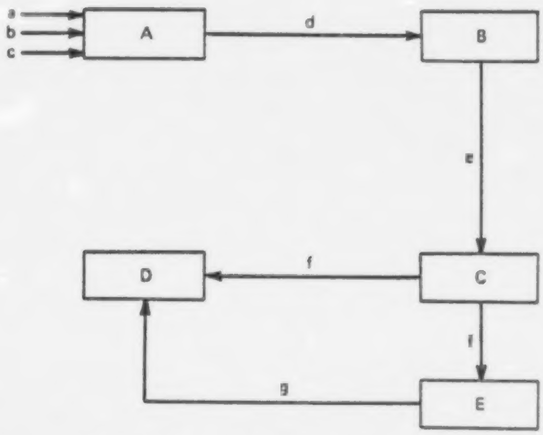

Fig. 3. A flow sheet for the large-scale production of slagceram. LEGEND: (a) slag; (b) sand; (c) nucleating agent; (d) slagceram glass; (e) shaped slagceram-glass article; (f) shaped slagceram article; (g) shaped slagceram article with special finish; (A) melting furnace; (B) shaping machinery; (C) heat-treatment furnaces; (D) shipping bay; and (E) finishing plant.

sions a shaping operation might be included at a point in the heat-treatment cycle where crystallization was not quite complete (the softening temperature of the uncrystallized material is much lower than that of the crystallized). The heat treatment could be used for simultaneously enameling articles to produce eg, specially chemically resistant surfaces or colors outside the normal range obtainable. Although the hardness of slagceram makes polishing an expensive operation, the product looks very decorative, and, since slagceram can be made in relatively thin sheets, might be competitive. The polishing would be carried out, probably with diamond paste, in a finishing shop, which would also contain the diamond wheels needed for cutting slagceram to special shapes or to specially close dimensional tolerances.

Properties of Slagceram

The main test program on the physical, mechanical, service, and chemical properties of slagceram was carried out on material nucleated with chrome ore and titania or iron oxide and made on the pilot-plant scale.

The apparent density, 2.9–3.0 Mg/m^3, is somewhat higher than that of the slagceram glass. The difference would have been greater but for the development of a small degree of porosity during crystallization. The total porosity, determined by microscopic measurements on cut sections, was about 10%, but only about 5% was open porosity (measured by the amount of water absorbed after holding of the test piece in vacuum). Very much lower values of open porosity have been observed. Observations on pore-size distribution were made on one batch of slagceram by the mercury-intrusion method at pressures up to 12.4 MN/m^2. Most pore sizes fell into the 0.1–0.3 μm and 50–100 μm ranges. These values were obtained if the pores were assumed to be cylindrical and the contact angle with mercury 140°. The specific heat at room temperature is 0.71 kJ/kg K, the coefficient of linear expansion 5×10^{-6}/K and the thermal conductivity (Lees Disc) 1.3 W/m K. The resistivity of slagceram is $10^{8.5}$ Ω-cm before, and $10^{7.9}$ after, a standard damp heat aging test in which the test piece is kept at 38–42°C and a relative humidity of 90–95% for four days.

The scratch hardness of slagceram on Mohs' scale is between 8 (topaz) and 8½ (emery); the indentation microhardness (Vickers diamond pyramid) about 750. Scratch resistance is probably a more valuable technical index. It was found by a modification of a test method used for paints, a load of 12.8 N being applied through a pyramidal diamond point resting on the specimen sliding beneath it. The average width of scratch produced on slagceram was less than half that on either glazed or quarry tiles. The excellent resistance of slagceram to abrasion and general wear has been demonstrated in service tests, some lasting over four years, eg, in coke chutes; relatively short tests on an industrial floor area exposed to the passage of heavy, steel-wheeled trolleys, radiation from a furnace that kept the average floor temperature at about 90°C, and spillage of molten slag, showed that slagceram was greatly superior to concrete and ceramic tiles. The coefficient of friction between steel and new slagceram tiles is considerably lower than that for unpolished new ceramic tiles, but equal to that for worn polished ceramic tiles. No quantitative information is yet available on how the friction coefficient of slagceram changes with continued wear.

In addition to the service tests and the laboratory friction test, two types of laboratory tests for resistance to abrasion were used. One is the Morgan-Marshall test, devised for testing refractories, in which the mass lost by the test piece under the action of a blast of fused-alumina particles is determined. The loss with slagceram is much less than that of granite, fusion-cast alumina, and fusion-cast basalt. Even incompletely crystallized, porous slagceram, though somewhat poorer than the basalt, was better than hard-fired firebrick or china-clay brick. In the second type of abrasion test the test piece is held under load against a rotating disc onto which an abrasive is being fed; the loss in weight after a set number of disc revolutions is determined. Two abrasives, one consisting of rounded sand particles, and the other of sharp corn-emery particles, were used and gave somewhat different results. With sand the weight loss for slagceram was about 50–70% of that for fusion-cast basalt and about 31–44% of that for granite. With corn emery the average of the range for slagceram showed no significant advantage over the basalt, but retained its former advantage over granite. An important point from the service aspect is whether the measured abrasion resistance is a characteristic of the surface layer (which would eventually be worn away) or of the bulk of the material. The tests with sand showed very little difference in weight loss from a chill-cast surface and from an internal, ground surface, but both were considerably less than from a surface cast exposed to the air.

The crushing strength of slagceram, measured on a standard 76.2-mm cube of slightly irregular shape, is approximately 207 MN/m^2. This would probably have been exceeded with a regular cube. Slagceram has good resistance to concentrated static loads, no measurable indentation being produced in several weeks by a load of about 2.3 kN applied through a steel sphere (ball bearing) 12.5 mm in diameter. The resistance of slagceram to concentrated impact loads measured by a standard method, in which a 4.54-kg weight with a rounded end is dropped repeatedly onto the test piece from increasing heights, was equal to that of ceramic floor tiles (failure at 50 mm). In general, the resistance of slagceram to impact is relatively good by ceramic, but not by metal, standards.

The modulus of rupture (bending test) of slagceram depends considerably on the method of preparation of test pieces as well as on the slagceram itself. For example, three-point-loading tests on pieces cut from a tile of annealed slagceram nucleated with iron oxide gave values of 107 ± 22 MN/m^2, those for annealed individually-cast rods being 135 ± 18 MN/m^2. The poorer values and large scatter for machined test pieces are in line with experience in the testing of glasses and ceramics, which are very liable to develop stress-concentrating surface imperfections during the machining process. The values for cast test pieces can therefore be taken as more representative of what can be expected from slagceram articles in service. In fact, with ceramic-type materials there is no completely satisfactory alternative to the use of complete articles as the test piece.

The properties quoted refer to slagceram in the massive state. Those of lightweight (foamed) slagceram have not been properly evaluated yet, but published values for the corresponding U.S.S.R. product (6) suggest that densities of 300–700 kg/m^3, compression-strength values of 6–14 MN/m^2 and thermal-conductivity values of about 0.13 W/m K would be obtainable.

The properties of slagceram specifically for building applications were also determined. The impervious nature of smooth slagceram makes adhesion to ordinary cement mortar rather poor; better results are obtained with rough surfaces. With a filled epoxide adhesive, however, a very strong bond is obtained even with smooth slagceram, failure occurring in the epoxide rather than at the interface. Slagceram has excellent long-term constant-temperature stability, the expansion observed being at the limit of sensitivity of the test method. Room-temperature tests lasting 12 weeks at 100% relative humidity on slagceram tiles that had been sprayed with suspensions of the spores of four of the more common molds affecting buildings showed that only isolated growths, which do not impair appearance, were present. Slagceram specimens have been exposed for over five years at a variety of atmospheric corrosion test sites covering the main aggressive types of atmosphere (urban, industrial urban, industrial marine) and at a test site where the specimen is immersed at high tide and exposed at low. In no case has any significant deterioration been observed.

The resistance of slagceram to various liquids has been compared with that of earthenware tiles. In concentrated and 50% sulfuric acid there is no difference between the materials; in 10% sulfuric and in concentrated and dilute (10%) nitric, hydrochloric and acetic acids the resistance of slagceram was less. In concentrated and 5% caustic soda and distilled water there was no difference between the two materials, and in 10% sodium carbonate, 5% ammonia, tap water, and 20% magnesium sulfate, slagceram had the higher resistance. The tests lasted two years for slagceram nucleated with chrome ore and titania and 6 months for slagceram nucleated with iron oxide. Long-term tests have shown that slagceram has good resistance to spillage of milk and beer.

It is impossible to compare the properties of slagceram precisely with those of the parallel products (slag sitalls) developed in the U.S.S.R. because test conditions have generally not been specified and discordant values have been quoted (possibly because they refer to different grades, or even to material made not from slag but from the expensive special glasses used for glass-ceramics). According to a publication (6), the mechanical properties appear to be similar to those of slagceram, except that the crushing strength of slag sitalls is said to be higher; slag sitalls have been formed into various articles, including tiles, sheet, corrugated sheet, pipe, electrical insulators, sanitary ware, and light-weight blocks; a range of colors can be produced. Production is believed to be on a large pilot-plant scale for tiles and sheet, and on a smaller scale for other shapes. The reported cost of slag sitalls, about \$39–\$67/tonne of sheet (7), are difficult to interpret because they depend on the doubtful meaning of the official ruble rate of exchange and because the rate of production they refer to—a dominant factor—is not specified.

Comparison with the Japanese materials is also difficult, but it appears that their bending strength is higher than those of either slagceram or slag sitalls (4).

Appendix 1. Conversion Factors

To convert	Multiply by
tonne (t) to short ton	1.10231
MN/m^2 to lbf/in^2 (psi)	145.04
N to lbf	0.22312
mm to in.	0.03937
μm to in.	0.03937×10^{-3}
kg to lb	2.20462
Mg/m^3 to lb/ft^3	62.43
kg/m^3 to lb/ft^3	62.43×10^{-3}
kJ/kg K to Btu/(lb)(°F)	0.23885
W/m K to $Btu/(hr)(ft^2)(°F/ft)$	0.5778

See Units in this volume.

Bibliography

1. S. Klemantaski and B. Kerrison, *Chem. Ind.* **15**, 1745 (1966).
2. M. W. Davies, B. Kerrison, W. E. Gross, M. J. Robson, and D. F. Wichall, *J. Iron Steel Inst.* **208**, 348–370 (April 1970).
3. I. I. Kitaigorodskii, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva* **8**(2), 192 (1963) T. E. Goliuf et al., Proizvodstvo shlakositallov, Vol. II, MPSM, Ukr.S.S.R., 1968.
4. U.S. Pat. 3,170,780 (Feb. 23, 1965), T. Takahera and A. Tsuji (to NGK Insulators Ltd.).
5. S. Klemantaski, *Steel Times Ann. Rev.* **1969**, 158.
6. I. I. Kitaigorodskii, 'Sitalls' in A. T. Tumanov, ed., *Encyclopedia of Modern Techniques*, Vol. 3 II, Izdatel'stvo Sovetskaya Entsiklopediya, USSR, 1965, pp. 169–171.
7. *Chem. Proc.* **12**, 78 (June 1966).

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SOLUBILITY PARAMETERS

Solubility parameter concepts have found wide and increasing use in many areas of industrial and academic endeavor because of the simplicity with which significant predictions can be obtained. These concepts are generally applied to solvent selection in the industrial community, while the calculation of solubilities and thermodynamic properties have concerned the more theoretical workers. Hildebrand's initial work was based on the solution of nonelectrolyte solids in nonpolar solvents, although such topics as gas-in-liquid solubility, liquid–liquid miscibility, metallic solutions, polymer solutions, and correlations with surface phenomena and critical properties were discussed (1, 2). Burrell (3–6) applied the solubility parameter to polar solvents and polar polymers, and Hansen (7–12) has described relationships with organic and inorganic pigments, proteins, and biological materials, and even inorganic salts. Based on these results, it appears that a solubility parameter study can provide systematic information on physical interactions for any material which interacts suitably (dissolves, swells, or absorbs) when contacted with a sufficient number of solvents (energy probes). It is assumed that there is a close similarity between the cohesive energy densities of the interacting, well-defined solvents and that of the substrate material, and thus a solubility parameter may be assigned to the material.

Historical Background

Hildebrand and Scott designated the energy of vaporization per cubic centimeter as the *cohesive energy density* (*ced*) and its square root as the *solubility parameter*, δ. Thus,

$$\delta = \left(\frac{\Delta H_V RT}{V}\right)^{1/2} = \left(\frac{\Delta E_V}{V}\right)^{1/2} = (ced)^{1/2} \qquad (1)$$

where ΔH_v and ΔE_v are the heat and energy of vaporization, respectively, and V is the molar volume. As suggested by Crowley (13) the unit $(\text{cal/cm}^3)^{1/2}$ is designated as a "hildebrand." This parameter is important in the estimate of the heat of mixing for two nonpolar liquids, given by Hildebrand as:

$$\Delta H^M \approx \Delta E^M = \phi_1\phi_2(x_1V_1 + x_2V_2)(\delta_1 - \delta_2)^2 \qquad (2)$$

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Reference 8

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GHT/JS

AIR MAIL

2 NOVEMBER, 1979

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Dear Bob,

Thank you for your letter of 18 October. The work on "Slagceram" was carried out some years ago by the former British Iron & Steel Research Association (now part of B.S.C's research organisation). Several years of intensive and detailed work on Slagceram were carried out.

I think the simplest definition of Slagceram would be a chemically modified blastfurnace slag into which nucleating agents have been added. The remelted product is formed and then heat treated to produce a controlled fine crystalline structure. The product has special properties, particularly in terms of abrasion resistance.

BISRA carried out work on the laboratory scale and also up to small pilot plant scale. Later the project was further investigated on the large pilot scale using a continuously operable glass melting tank equipped with "gobbing" facilities. At the later stage the work was organised and financed by the then United Steel Co. and another external company. It was at this stage that I became actively involved.

As originally conceived the Slagceram project aimed at producing a slag based "pyroceram" type material. However, early work indicated that the production of pyroceram type structures was impossible and work was concentrated on achieving fine grain structures which were, nevertheless, resolvable under the optical microscope. Chemical modification was aimed principally at increasing the SiO_2 content and introducing nucleating agents.

The large pilot scale venture revealed problems in achieving uniform temperature conditions in the melt and also indicated rapid changes in melt viscosity with temperature. This resulted in considerable difficulty in "gobbing". These problems would not necessarily follow if different processing routes were followed.

I think it is worth mentioning that the Russians have put considerable resources into a project to produce "Sittalls". I gather they have had commercial scale plants running on this material but it must always be remembered that they work under a different form of commercial constraint.

/Cont'd.

To sum up, Slagceram is technically a most interesting material with special properties which could be of considerable use in a number of areas. There are technical problems which need to be dealt with if continuous production is to be realised but the likely major problem is cost. There is a first melting stage, followed by forming and annealing and then the final heat treatment. B.S.C. stopped further work on the project some years ago but there is considerable know-how available within B.S.C. for potential clients interested in this product.

It may be useful for you to know that Dr Phil Rogers at Imperial College, London University, a member of the original Slagceram team, has been working on modified formulations. His aim is to simplify the process and improve the product. It may be worth having a word with Phil if you have an interest in this area.

I would emphasise that Slagceram is a specialist ceramic type material. There could well be other ceramic forms in which your enquirer may be interested, into which slags could be introduced.

Attached are copies of three papers which should give you some background into the technology.

Many thanks for your felicitations. I am fit and well and leave for two weeks' holiday in Italy in two weeks' time. My best wishes to you and your wife.

Yours sincerely,

GEORGE H. THOMAS

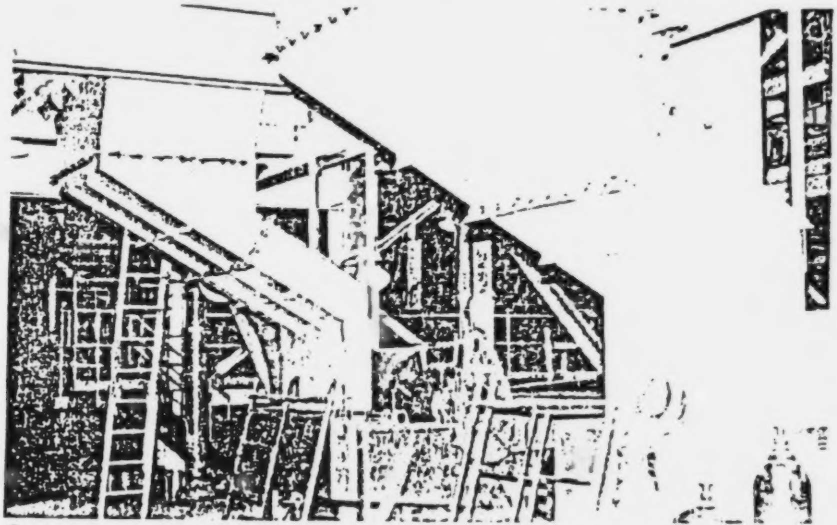
South Kensington
Exhibition Rd. (10 mt.)
left. Prince Consort Rd.
Dept. of Metallurgy, Royal School of Mines
(1st entrance on left).
go in thru G05

Appendix B

R Hancock PEng
Manager — Canada West
Canadian Stebbins Engineering & Mfg Ltd

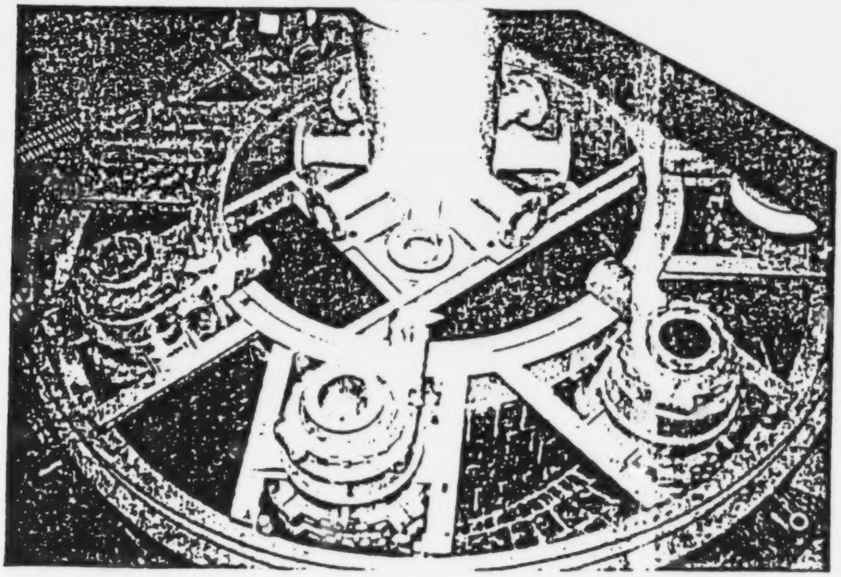
Reduce maintenance and production downtime using wear-resistant ceramics

The Mining Industry processes large volumes of ore tailings and other abrasive materials resulting in extensive wear to equipment and transfer systems. Maintenance costs and more importantly, lost production time required for replacements have shifted the emphasis in materials selection for modern processing systems. The focus is on materials with moderate to high resistance to abrasion and impact as well as mild corrosion resistance.



Coal slurry chutes. Sides and bottom quarry tile laid in Rubex, a latex rubber based mortar

Cyclopac linings. Distribution chamber prefabricated with basalt lining. Reject channel basalt tile laid in polyester resin mortar. Centre accepts collector quarry tile laid in Rubex, a latex rubber based mortar



Mining systems use three basic types of materials

1. Abrasion resistant metallic alloys
2. Resilient organic materials such as rubber and urethanes
3. Hard non-metallics such as vitrified clay, basalt and aluminum oxide.

It is this last group which has seen a dramatic increase in its use over the last few years. Compared to other alternates, these non metallics have extended the service life of piping, cyclones, chutes, launders and similar equipment three to twenty times.

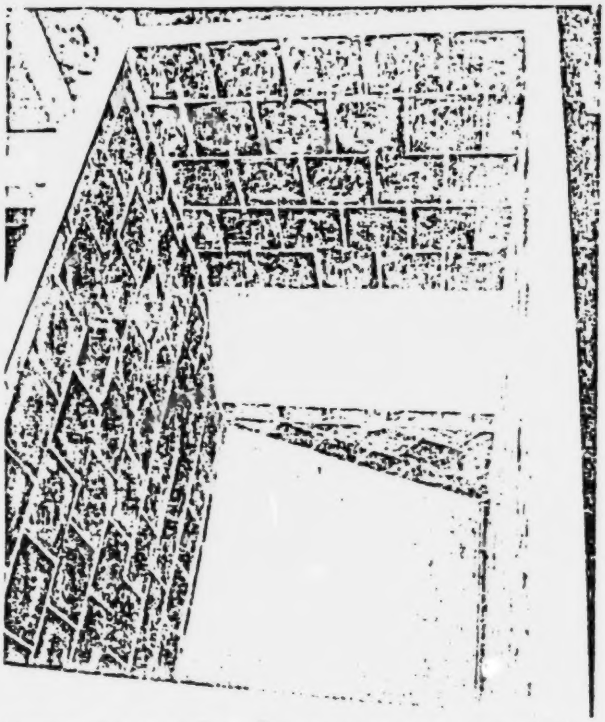
The first major project in North America to use basalt and quarry tile in the original design of their mining process systems has been Quintette Coal in British Columbia. The Union Coal Plant at Obed Marsh, Alberta, chose quarry tile and alumina in their design. After several years of operation Victoria Coal in Nova Scotia rebuilt their process systems using these same ceramics.

TILES

Vitrified Clay Tiles are most commonly used as 150x150x16 quarry tile. For maximum abrasion resistance only vitrified tiles with a mean water absorption of less than 1% should be used. These tiles have moderate wear resistance but offer excellent chemical resistance, particularly to acids and chlorides, which makes them a good selection for waste water systems. They are an economical liner system for processed coal and other fine aqueous slurries and can easily be cut to line a large variety of shapes.

Cast Basalt Tile. Basalt rock is melted, cast into shapes and annealed to form a finely crystallized glass. Abrasives passing over basalt gradually give the tile a high polish which reduces friction and wear. Basalt offers excellent abrasion resistance and performs well at temperatures up to 400 C. It has limited impact and thermal shock resistance, a factor to be considered in systems design. Generally basalt is ideal for lining equipment handling abrasive solids in liquid suspension. It has given excellent service in such diverse areas as coal processing chutes, pump boxes and cyclopacs, dredging chutes, ore hoppers, shale handling chutes, ash hoppers, and sluices and wood chip handling system

Material	Hardness (Mohs)	Coefficient of Friction dry	wet
Alumina	9	0.25	
Basalt as cast	8.5	0.40	0.38
Basalt polished by service		0.27	0.28
Ni Hard	8	0.42	0.45
Quarry Tile	7.5	0.42	0.45
Glass — new	5.5	0.23	0.28
— scratched		0.38	0.39
Stainless steel	5	0.29	0.32



Heavy circuit coal chute. Basalt tile laid with silica-filled polyester mortar

As basalt is also provided as a lined pipe system, it has been used extensively in coal and ash handling systems.

High Density Aluminum Oxide: pressed or slipcast ceramic bodies containing 85+% aluminum oxide. They are fired at 1500+ degrees C producing an extremely dense hard body with a smooth surface finish. The tiles have excellent chemical resistance and can be used at temperatures up to 1100°C. However, they have low thermal conductivity which can lead to spalling, if thermal shock is encountered.

With high physical strength, alumina tiles have good impact resistance. The tiles are installed at thicknesses from 6mm to 50mm, depending on the impact expected. The tiles can be shaped or cut to fit any irregular areas. Alumina tiles are used in the most demanding wear and impact areas. Where alloys last only months, alumina will often give years of service.

Typical applications of alumina tiles include cyclone cleaner systems, iron ore, coke and sinter-handling, centrifuge ning, wood chip separator cyclones, and an casings and blades.

MORTARS

Mortars are critical to the performance of any of these liner systems as the selected adhesive or mortar must perform in the same media as the tiles. A variety of adhesives each with distinctive properties suitable to the application are available.

Portland Cement. High strength Portland Cement base mortars find extensive use with basalt piping and clay tile. Other mortars are usually used for joints to isolate the cement from the erosive media. Portland Cement mortars have low bond strength to steel substrates.

Latex Rubber based mortars offer good substrate adhesion without extensive surface preparation. They also offer some resilience to substrate movement. They are most commonly used with quarry tile up to 60 C and are the most economic method of installation.

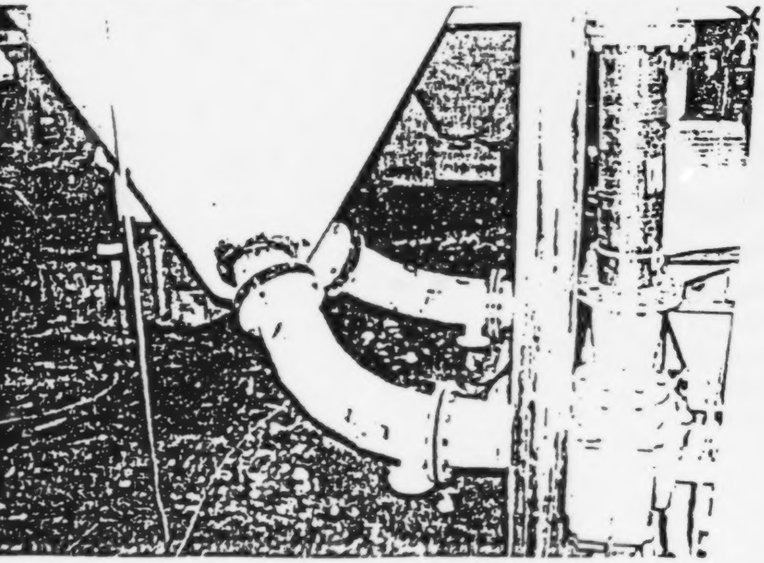
Epoxy Resin Mortars. Many different resin bodies are available with widely varying properties and they are filled with alumina or silica materials. Epoxies have high structural and bond strengths, good chemical resistance and are used up to 140 C. They are most suitable with alumina, basalt and quarry tile systems.

Polyester Resin Mortars. Many different resin bodies are available. These are most often silica filled and give good abrasion resistance. Where required, resins can be selected with excellent chemical resistance and are not normally used at temperatures above 100 C. Polyester resin mortars are the most economic selection for installation of basalt tiles.

Furan Resin Mortars have high structural and bond strengths as well as good chemical resistance. They are somewhat more expensive than other resin mortars, but are used when temperature resistance to 300 C is required.

Silicate Mortars are based on calcium or potassium silicates. They offer temperature resistance to 1000+ degrees C. They are commonly used with

Cone shaped pump box. Cone: basalt tile laid in polyester resin mortar. Piping: Basalt lining elbow prefabricated, nozzle on cone fitted and lined in place



alumina tiles in high temperature systems such as those found in coal fired power plants

INSTALLATION METHODS

Proper installation methods are the key factors in the performance of these process systems. Mortars require proper mixing, handling and curing temperatures. Surface preparation required varies with the material selected. Tiles are cut, fitted and shaped to ensure that joints widths are kept as thin as is practical.

These wear resistant ceramic materials have substantially extended the service life of equipment operating under very difficult conditions. The increase in production efficiency due to reduced down time and the reduction of prime time maintenance costs result in major economic benefits from the use of these lining materials.

Canadian Stebbins is a specialty contractor offering design, material supply and site installation for a wide variety of brick and tile lining systems.

Technical information for this article has been provided by Paul Verhay of the industrial ceramics division of Williams and Wilson Ltd.

Volume

2

REQ NO. 4-9196

OFFICE OF TECHNOLOGY
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CANMET
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CANMET

[redacted]

MARKETING STUDY
FOR ABRASION RESISTANT CERAMIC TILES
PHASE II

CONTRACT REPORT NO OGT 84-00310

for:

Energy, Mines and Resources Canada

Canadian Centre for Mineral and Energy Technology (CANMET)

Consultant: Marvin Ryder, B.Sc.(Hons), B.A., M.B.A.

McMASTER UNIVERSITY SMALL BUSINESS
CONSULTING SERVICE

Hamilton, Ontario

The S.B.C.S. is sponsored by
THE MINISTRY OF INDUSTRY AND TRADE
GOVERNMENT OF ONTARIO

46 pp

MICROMEDIA

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1.0 Introduction

Research has been conducted by the Ontario Research Foundation and the Canada Centre for Mineral and Energy Technology to develop an abrasion-resistant glass-ceramic tile for use in material handling systems. Slag is a principal component of this tile.

During July and August 1984, the Small Business Consulting Service (SBCS) conducted a marketing study on the abrasion-resistant ceramic (ARC) tile market. The study revealed that the Canadian market for ARC tiles was $4-6 million and the U.S. market was approximately ten times larger with sales of $50-60 million annually.

This report follows up on the initial work by comparing the three types of available ARC tiles to find potential market penetration strategies for the CANMET-ORF tile. Further, the attributes that an ARC tile should possess are examined using the results of a survey conducted with distributors and contractors of ARC materials. Besides using the ARC material to produce an ARC tile, four other uses for the material are presented here.

The report is presented in three parts:

Part I Survey Research
Part II Delphi Procedure to Isolate Other Uses
Part III Four Other Possible Uses for the ARC Material

Part I -- Survey Research

A three page survey was designed primarily to find out four things: 1) What attributes should an ARC tile possess ?; 2) How do people responsible for buying and selling ARC tiles rank these attributes ?; 3) How do the three types of ARC tiles (Cast Basalt, Alumina Oxide, and Silicon Carbide) rank on these attributes ?; and 4) Are there any strategic weaknesses that can be capitalized by a new ARC tile entrant ?

Two other types of questions were asked. One set was posed to verify information gleaned from earlier interviews. The other set asked about the manner in which tile purchases were made.

When Phase I had been conducted on the phone, the researcher perceived some annoyance on the part of the interviewees. For this research, the questionnaire was mailed to a list of ARC tile distributors and contractors who specialize in projects that have called for the use of ARC tiles.

It must be noted that the list of respondents for this work was very small. Only three ARC tile distributors could be found in Canada and the number of contractors found was only eight. Though this seems to be a small sample, it probably represents a census of opinions in Canada. The United States was not included in the sample for two reasons: 1) lack of information on addresses of tile distributors and contractors; and 2) applicability of the survey to the American environment. Further it was assumed that any company purchasing the ARC technology would attempt to find a market in Canada first before branching to the U.S.

The response rate for this research was excellent with all three distributors and five of the contracting firms returning their survey forms.

The survey is presented on the next three pages followed by the analysis of the results.

ABRASION-RESISTANT CERAMIC TILE MARKETING: A STUDY

For the purposes of this survey, we are using the term "abrasion-resistant ceramic tile" to describe any tile made from cast basalt, alumina oxide or silicon carbide used in an abrasive environment to reduce wear.

Section 1 Definition of Abrasion-Resistant Ceramic Tiles

In order to better understand the marketing of Abrasion-resistant Ceramic tiles, we would like to know something about your past tile purchases. Please complete the following questions by placing a check in the box ☑ which corresponds to your answer.

1. When choosing an Abrasion-resistant Ceramic tile, how important are the following factors in making your decision to buy a specific type of tile. Please put a checkmark in the box ☑ which indicates your opinion of the degree of importance from Very Important to Of No Importance.

	VERY IMPORTANT	IMPORTANT	SLIGHTLY IMPORTANT	OF NO IMPORTANCE
Abrasion Resistance	☐	☐	☐	☐
Thermal Shock Resistance	☐	☐	☐	☐
Price	☐	☐	☐	☐
Weldability	☐	☐	☐	☐
Castability of ARC Material	☐	☐	☐	☐
Variety of Sizes	☐	☐	☐	☐
Variety of Thicknesses	☐	☐	☐	☐
Colour	☐	☐	☐	☐
Canadian Made	☐	☐	☐	☐

2. From which of the following types of suppliers do you make most of your Abrasion-resistant Ceramic tile purchases ?

☐ 1. TILE MANUFACTURER

☐ 2. TILE WHOLESALER

☐ 3. INDUSTRIAL CONTRACTOR

☐ 4. OTHER (Please Specify)________________________

3. From what companies have you made Abrasion-resistant Ceramic Tile purchases?

   ☐ CARBORUNDUM CORPORATION (PACKO CORP.)

   ☐ CHAMPION SPARKPLUG

   ☐ COORS PORCELAIN

   ☐ DIMONITE

   ☐ FERRO CORPORATION

   ☐ OTHERS (Please Specify) ____________________

   ____

   ____

4. We would like to know your opinions about various types of Abrasion-resistant Ceramic Tiles. Below are a series of statements related to Abrasion-resistant Ceramic Tiles. Consider each type of tile separately and evaluate the statement using the rating scale given below.

2	1	0	-1	-2
AGREE	SLIGHTLY AGREE	INDIFFERENT	SLIGHTLY DISAGREE	DISAGREE

Please place the number corresponding to your evaluation in the box provided |-1|. If you have no opinions about a type of tile leave the column blank.

	CAST BASALT	ALUMINA OXIDE	SILICON CARBIDE
The tile price was high.	☐	☐	☐
The tile was Canadian-made.	☐	☐	☐
The tile was not weldable.	☐	☐	☐
The tile was thermal shock resistant.	☐	☐	☐
There was not a variety of thicknesses.	☐	☐	☐
The tile had good abrasion-resistance.	☐	☐	☐
The ARC material was castable.	☐	☐	☐
The tile colour was appropriate.	☐	☐	☐
There was not a variety of sizes.	☐	☐	☐

Section 2 How You Buy Abrasion-Resistant Ceramic Tiles

1. Approximately how much did your company spend last year on Abrasion-resistant Ceramic Tile purchases?

   ☐ 1. LESS THAN $25,000

   ☐ 2. FROM $25,000 TO $49,999

   ☐ 3. FROM $50,000 TO $74,999

   ☐ 4. FROM $75,000 TO $99,999

   ☐ 5. $100,000 OR MORE

2. Approximately how many kilograms of Abrasion-resistant Ceramic Tiles has your company bought in the past twelve months ?

   ☐ 1. LESS THAN 2,500 KILOGRAMS

   ☐ 2. FROM 2,500 TO 4,999 KILOGRAMS

   ☐ 3. FROM 5,000 TO 7,499 KILOGRAMS

   ☐ 4. FROM 7,500 TO 9,999 KILOGRAMS

   ☐ 5. 10,000 KILOGRAMS OR MORE

3. Which of the following statements best describes the manner in which Abrasion-resistant Ceramic tile purchases are made by your firm ? (Check only one).

   ☐ 1. WE CALL A PREVIOUS SUPPLIER

   ☐ 2. WE CALL ONE OR MORE POTENTIAL SUPPLIERS AND ASK FOR QUOTATIONS

   ☐ 3. WE USE A SPECIFIC SUPPLIER AS REQUESTED BY A CLIENT

4. Which of the following describe the ways in which you acquire information about Abrasion-resistant Ceramic tiles ? (Check all that apply).

   ☐ 1. SUPPLIER SALESPEOPLE

   ☐ 2. MANUFACTURER CATALOGUE

   ☐ 3. WORD OF MOUTH

   ☐ 4. TRADE MAGAZINE ADVERTISEMENTS

   ☐ 5. TRADE SHOWS

5. Please go back to question 4 and circle the information source ☑ you checked which is the most important.

Analysis of the Survey Response

Rather than listing responses on a percentage basis, the actual number of responses will be listed. This is viewed as the most responsible method of reporting small numbers.

Attributes of ARC Tiles

Question 1 from the survey addressed this issue specifically. The responses are shown below.

1. When choosing an Abrasion-resistant Ceramic tile, how important are the following factors in making your decision to buy a specific type of tile.

	VERY IMPORTANT	IMPORTANT	SLIGHTLY IMPORTANT	OF NO IMPORTANCE
Abrasion Resistance	8	0	0	0
Thermal Shock Resistance	0	0	3	5
Price	6	2	0	0
Weldability	0	4	4	0
Castability of ARC Material	0	0	3	5
Variety of Sizes	5	3	0	0
Variety of Thicknesses	5	3	0	0
Colour	0	0	1	7
Canadian Made	0	0	1	7

These responses allow a ranking of the attributes in order of importance.

Ranking	Attribute
1	Abrasion Resistance
2	Price
3	Variety of Sizes
3	Variety of Thicknesses
5	Weldability
6	Thermal Shock Resistance
6	Castability
8	Colour
8	Canadian Made

It is obvious from this list that the first four attributes are very important for the success of an ARC tile. It is also interesting that Thermal Shock Resistance, Castability and Canadian Made are not viewed as being very important. These are some of the features that the CANMET-ORF ARC tile has to offer.

Comparison of ARC Tiles

Question 4 asked the respondents to compare each of the three types of tile presently available on the attributes listed above. The responses given below are the average of the scores given by the respondents. It should be noted that all eight respondents were able to compare Cast Basalt and Alumina Oxide but only five felt qualified to consider Silicon Carbide.

4. We would like to know your opinions about various types of Abrasion-resistant Ceramic Tiles. Below are a series of statements related to Abrasion-resistant Ceramic Tiles. Consider each type of tile separately and evaluate the statement using the rating scale given below.

2	1	0	-1	-2
AGREE	SLIGHTLY AGREE	INDIFFERENT	SLIGHTLY DISAGREE	DISAGREE

	CAST BASALT	ALUMINA OXIDE	SILICON CARBIDE
The tile price was high.	-1.5	1.0	2.0
The tile was Canadian-made.	-1.9	-1.9	-2.0
The tile was not weldable.	-1.0	-1.4	1.2
The tile was thermal shock resistant.	-1.6	-1.5	-1.6
There was not a variety of thicknesses.	0.4	-1.6	0.6
The tile had good abrasion-resistance.	0.8	1.6	2.0
The ARC material was castable.	-1.9	-1.8	2.0
The tile colour was appropriate.	0.4	0.4	0.2
There was not a variety of sizes.	0.0	-1.6	0.4

There are many interesting features to be found in the responses above. The respondents do not perceive any difference between the three types of tile in their colour (slight liking), thermal shock resistance (poor) and Canadian origin (not Canadian made). Respondents also recognized the castability of silicon carbide and poor castability of cast basalt and alumina oxide.

How Tile Purchases Are Made

Five questions were asked to determine how tile purchases were made.

2. From which of the following types of suppliers do you make most of your Abrasion-resistant Ceramic tile purchases ?

4	1. TILE MANUFACTURER
6	2. TILE WHOLESALER

This result is not surprising as three of the respondents were tile distributors while five of the respondents were contracting firms. It is rare for a contracting firm to deal directly with a manufacturer.

3. From what companies have you made Abrasion-resistant Ceramic Tile purchases?

1	CARBORUNDUM CORPORATION (PACKO CORP.)
2	CHAMPION SPARKPLUG
4	COORS PORCELAIN
1	FERRO CORPORATION
6	WILLIAMS & WILSON
3	THERMALLOY

Again few of the manufacturers were dealt with directly. Earlier information seems to be confirmed here that Coors Porcelain and Champion Sparkplug in the United States are the dominant players in the manufacturing market. From a distribution standpoint, Williams & Wilson in Canada seem to be the dominant distributor having dealt with each of the contracting companies.

3. Which of the following statements best describes the manner in which Abrasion-resistant Ceramic tile purchases are made by your firm ?

7	1. WE CALL A PREVIOUS SUPPLIER
1	2. WE CALL ONE OR MORE POTENTIAL SUPPLIERS AND ASK FOR QUOTATIONS

This question highlights the loyalty of both distributors and contractors to former suppliers. Though price is important, the dependability of past suppliers is apparently a telling factor when deciding from whom to purchase tile.

Respondents perceived price differences between the three products with prices appearing to increase from cast basalt to silicon carbide. This price difference does appear justified as the perceived abrasion-resistance also increases along the same dimension.

It was generally perceived that cast basalt and silicon carbide tiles were limited in sizes and thicknesses available whereas alumina oxide tiles were perceived as being available in a wide variety of sizes and thicknesses. Both cast basalt and alumina oxide tiles appear to come in weldable varieties but silicon carbide tiles seem to be limited in this capacity.

Implications for Market Strategies

Using the attribute ratings and comparisons of the three tiles some important strategic implications can be seen.

First, companies using ARC tiles do not seem to consider thermal shock resistance, colour or Canadian origin when purchasing tiles. Second any marketing strategy must focus on abrasion resistance, price and variety of sizes and thicknesses to be successful.

It would appear that cast basalt is the most vulnerable to an attack. If the price of the CANMET-ORF tile was comparable to cast basalt while the abrasion resistance was closer to that of alumina oxide, the tile should be able to capture a significant share of the cast basalt market. Further, if the new tile could be produced in more sizes and thicknesses than cast basalt, the battle would be easier to fight.

Silicon Carbide is also vulnerable to attack. It is perceived as being expensive and limited in its sizes and thicknesses. If the CANMET-ORF tile could be castable yet priced close to cast basalt and available in a number of sizes and thicknesses, there is a good possibility of taking some of this market away. With only five companies evaluating silicon carbide, two other factors come to light. 1. Knowledge of silicon carbide is limited so a new tile properly promoted could be accepted by "ignorant" firms. 2. Silicon Carbide is probably used for special projects only where alumina oxide tiles will not do (ie. pipe joints). If a more general product can do what a specialized product can do and more, the specialized product is especially susceptible.

The least vulnerable of the three types of tile is the alumina oxide. Though its price is viewed as somewhat high, it does come in a wide range of sizes and thicknesses and does provide good abrasion resistance. It's only weak spot is the price dimension. If the CANMET-ORF tile is comparable in abrasion resistance and cheaper then some inroads might be made. There is probably a lot of dealership loyalty so the fight here will centre on lining up distributors for the product and convincing them to push the product line. This is much more difficult to do.

4. Which of the following describe the ways in which you acquire information about Abrasion-resistant Ceramic tiles ?

   8 1. SUPPLIER SALESPEOPLE

   8 2. MANUFACTURER CATALOGUE

No other sources of information where checked. All companies seem to rely on supplier salespeople and manufacturer catalogues for their information. The follow-up question was more telling as respondents were asked to circle the most important source of information. This recast question 4 as follows.

4. Which of the following describe the ways in which you acquire information about Abrasion-resistant Ceramic tiles ?

   6 1. SUPPLIER SALESPEOPLE

   2 2. MANUFACTURER CATALOGUE

The influence of supplier salespeople is especially significant. Thus for any new product coming on the market, the support of exisiting distributors is crucial for success.

Other Information

Two questions were asked to help verify information reported in Phase I.

1. Approximately how much did your company spend last year on Abrasion-resistant Ceramic Tile purchases?

   1 3. FROM $50,000 TO $74,999

   3 4. FROM $75,000 TO $99,999

   4 5. $100,000 OR MORE

The dollar ranges used here were suggested to the researcher by a contracting firm during a pre-test of the questionnaire. Unfortunately, the actual responses appear to fall outside of the ranges used. This leads one to the obvious conclusion that contractors deal on a much smaller scale than distributors. It is probably safe to assume, however, that the dollar size of the market for ARC tiles is lower than that initially reported. The $4-6 million dollar figure probably included installation charges. In Canada, the actual amount spent on ARC tiles is probably in the $1-2.5 million dollar range.

2. Approximately how many kilograms of Abrasion-resistant Ceramic Tiles has your company bought in the past twelve months ?

4 1. LESS THAN 2,500 KILOGRAMS

1 2. FROM 2,500 TO 4,999 KILOGRAMS

1 3. FROM 5,000 TO 7,499 KILOGRAMS

1 4. FROM 7,500 TO 9,999 KILOGRAMS

1 5. 10,000 KILOGRAMS OR MORE

This question was asked to get some idea of the size of the market in kilograms. Though each respondent answered the question, four noted that they found the question difficult to answer as they did not order tile by the kilogram but by the number required at a certain dollar figure.

The figures listed above would suggest an annual market for ARC tiles in Canada of between 25 to 40 tonnes. The accuracy of that figure though is somewhat questionable.

CONCLUDING COMMENTS

The survey indicates that the CANMET-ORF tile can succeed if it can be produced at a low price and high relative abrasion resistance. Pursuit of thermal shock resistance or castability properties seems to gain very little competitive advantage for the product.

It was noted earlier that respondents placed little importance on the product being Canadian made. As no product is produced in Canada, these people have never really had to consider this factor before. If the technology is implemented here, it would be wise to lobby provincial governments (who have control of Hydro facilities) to see if they would enforce a "Buy Canadian" policy. If this can be done, a non-competitive factor could be turned into a competitive advantage.

Part II Delphi Procedure to Isolate Other Uses

In attempting to find other uses for the CANMET-ORF A.R.C. material, it was felt that those most familiar with the project had, from the outset, been committed to its use specifically as an abrasion-resistant ceramic tile. To widen the list of possible uses, it was necessary to involve a large group of materials experts. Further, it was decided to use a Delphi procedure to compile a list of the three to five most promising ideas.

The Delphi procedure is an iterative one in which convergence of ideas is stressed. For this work, the procedure was a relatively simple one. In step one, a one-page description of the product was circulated to a panel of ten materials experts (including Ken Bell and Mark Van Roode and four professors from the McMaster Faculty of Engineering). They were asked to be creative and list any and all possible uses for the material that they could dream up. At the end of this step, a list was compiled of all mentioned uses.

In step two, the list of uses drawn up by the experts was circulated back to them. This time they were asked to list what they believed were the top five uses for the material. They were asked to make their judgements on the basis of market size, synergy with an A.R.C. tile manufacturer, competitive advantage and market growth. These responses were compiled and a much shorter list was generated.

Finally, in step three, the shorter list was again circulated and the panel was asked to list what they believed were the top three uses for the material. They were asked to make these decisions based on the same criteria as in step two. From this final list, the top four ideas were chosen for further investigation in Phase III.

On the pages that follow in this section, one can find: 1) the first letter and description of the product; 2) the second letter and initial list of possible uses; 3) the third letter and second list of possible uses; and 4) the final list of possible uses rank ordered to show the top four that will be investigated further in the next section.

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Faculty of Business

Marketing and International
Business Area

November 1, 1984.

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Dear ^:

Thank you for agreeing to help with this project. As you know, I am using a Delphi procedure to try and isolate possible uses for a new material developed by Energy, Mines and Resources Canada.

On the following page, you will find a description of the material in question. I would like you to read the description through carefully and then let your mind wander and be creative. Write down on a sheet of paper any possible uses you can think of for the material. Do not worry about the applicability of the idea or the commercial potential. Feel free to make any assumptions necessary for this work.

Though I do not want you to be constrained by time, I would like to compile all the responses before the end of the month. Please place your pages in the mail, using the return envelope provided, no later than November 15, 1984.

Once again, let me thank your for participating in this first stage of this work. You should receive a second letter from me, first thing next month.

Yours Sincerely,

Marvin Ryder.

MGR/pw

Description of the Material

A group of engineers working for Energy, Mines and Resources have developed a glass-ceramic material using iron blast furnace slag from DOFASCO in Hamilton. The material is, in essence, produced by modifying blast furnace slag through the addition of sand and some nucleating agents. The material is then heat treated to achieve appropriate crystal growth. At this point the material resembles any other glass-ceramic. It can be cast into moulds and treated further. It can be foamed to produce a more porous and light material. In essence, anything that can be created from a glass-ceramic can be created from this "slag-ceramic".

Listed below is a table of properties and preparation steps in the manufacture of slag-ceramics.

Table 1 Preparation and Properties of Slag-Ceramics

Composition:	Slag: 70.9 - 73.0%
	Sand: 21.5 - 22.3%
Or	TiO_2/Cr_2O_3: 4.4% /0.4%
	Fe_2O_3/C : 1.5 - 4.3% /3.5%
Melting Parameters:	1440°C for 45 min - 5 hrs
Thermal Expansion:	$6.41 - 9.54 \times 10^{-6}/K$
DSP:	725 - 775°C
Nucleation:	720°C/10 hours
Crystallization:	900°C / 3 hours
MOR:	8000 psi
Abrasion Resistance:	twice quartzite

Among the desirable properties slag ceramics possess are: 1) Excellent abrasion-resistance; 2) scratch hardness of between 7 and 9 on the Mohs scale; 3) good resistance to chemicals (fire-resistant) and weather (resists freezing damage); and 4) a high crushing strength. To the negative, it appears that slag ceramics are susceptible to thermal shock.

The slag-ceramic material has a brownish-gray colour but additives have been employed to give the material different colours including white, red, blue, green, gray and orange. The material, when cast, is so hard that polishing requires considerable time and effort.

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November 30, 1984.

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Dear ^:

Thank you for the excellent responses to my first letter. On the next page you will find a list of all possible uses that were suggested by the panel. I should point out that many of you suggested the material be used to produce an Abrasion-Resistant Ceramic Tile. This use has already been documented and it is my task to consider other uses beyond this. For that reason, "Abrasion-resistant Ceramic tile" has been dropped from the list.

At this stage, I would like you to examine the list of possible uses and submit to me what you consider to be the five best. In determining which uses are better than others, I would like you to keep four criteria in mind: 1) Size of the market; 2) Future growth of the market; 3) Competitive advantage; and 4) Synergy with an A.R.C. tile manufacturer.

The last point is important as any uses that I submit must be compatible with the markets and manufacture of A.R.C. tiles.

Please return your list of five uses in the return envelope provided. Though I know this time of year is a busy one, could you please have them in the mail by December 15, 1984.

Thanks for your help.

Yours Sincerely,

Marvin Ryder.

MGR/pw

Initial List of Possible Uses for A.R.C. Material

Abrasion-Resistant Ceramic Tiles (in future iterations this consideration
was dropped for obvious reasons)

Pavement Blocks
Pre-formed curbs and gutters
Wall panels for external facings
Partition panels for internal use
Pre-fabricated balconies and enclosures
Window Ledges
Floor Tile
Stair steps
Corrugated Roofing
Sanitaryware such as urinals, sinks, commodes
Technical instruments sych as crucibles, pestels, etc.
Silo Staves
Granaries and grain elevators
Insulation from foamed slag-ceramic
Decorative Tile for Bathrooms or home use
Kitchenware as in "Corningware"
Use in Mobile Home construction
Used for pipelines in extreme temperatures
Pipes for carrying slurries and dusts
Military applications in missiles
Nose cones for airplanes
External lining for ocean going vessels
Fence Posts
Breakwater material
Ball Bearings and bearings in general
Coatings for metals
Brake Shoes
Cutting guides and platens

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Marketing and International
Business Area

January 2, 1985.

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Dear ^:

Thank you for your responses and you will be pleased to know that we are into the final round of this work.

On the following page is the list of uses that the panel identified as more promising. I would like you to again review the list to determine what you believe to be the top three uses for the A.R.C. material. The uses listed on the next page are ordered by frequency of response (ie. the most frequently mentioned is listed first, etc.).

Again I would like you to use the four criteria that we used last time. Namely: 1) Size of the market; 2) Future growth of the market; 3) Competitive advantage; and 4) Synergy with an A.R.C. tile manufacturer.

Please return your list in the stamped envelope provided. Your responses should be sent no later than January 20, 1985.

Thanks for all your help with this work.

Yours Sincerely,

Marvin Ryder.

MGR/pw

List for Use in Step Three

It should be noted that the number of people who suggested each use was not revealed to the panel.

Use	Number Suggesting
Floor Tile	10
"Foam-type" insulation	7
Sanitaryware	6
Kitchenware	4
Piping	4
Missile/airplane nose cones	3
Pavement Blocks	2
Brake Shoes	1
Breakwater material	1
Ball Bearings	1
Metal Coatings	1

Final List of Possible Uses

At this stage two of the panel of ten chose not to respond further.

Use	Number Suggesting
Floor Tile	8
"Foam-type" Insulation	6
Sanitaryware	4
Missile/airplane Nose Cones	4
Kitchenware	2

Part III Four Other Possible Uses for the A.R.C. Material

From Part II, the four most promising uses for the material were: 1) Floor Tile; 2) "Foam-type" insulation; 3) Sanitaryware; and 4) Nose cones for aircraft and missiles. Each of these uses will be investigated in some detail below.

In particular, the analysis will focus on market size in dollars and units, the types of products available, the different target markets for the products, major players in the Canadian market and key success factors. The work is intended to provide an overview of the market for each product and some details have been omitted from this first cut accordingly.

FLOOR TILE

Besides Abrasion-Resistant Ceramic Tile, the tile market in Canada is divided between four other types: Floor Tile, Wall Tile (Maple Leaf Ceramics of Montreal produces 5 million square feet of wall tile annually), Bathroom Tile and Mosaic Ceramic Tile. In 1984, the amount of tile sold in Canada amounted to 115 million square feet. Dollar sales figures are unavailable. The abrasion-resistant ceramic material seems most appropriate for use as floor tile or, as it is sometimes known, quarry tile. In fact both the Russians and the British report using A.R.C. material in this way.

Quarry tile is usually brown in appearance and comes in both glazed and unglazed varieties. Quarry tile is semi-vitreous and very dense which makes it ideal for use in high traffic areas. Recently, coloured (green, blue, red and white) and patterned quarry tile have entered the market from foreign producers. However, most commercial projects still require the unglazed brown quarry tile only.

In Canada, only one company produces quarry tile. Clifton Ceramic Tile Inc. (or Frontenac Tile) is located in Kingston, Ontario. It produces about 3 million square feet of quarry tile annually to help satisfy Canadian demand. It should be noted that Canadians annually use 11.5 million square feet of quarry tile. The quarry tile that Clifton produces is sold primarily to commercial users for industrial floors, shopping centres and lobby areas.

Quarry tile purchases are usually quite large. An average mall may need 100,000 square feet of quarry tile to cover its floor. Quarry tile is also very expensive. A sample price chart is included below.

Sample Prices for Quarry Tile

Size	Price
2" x 2"	$3.20
4" x 4"	$3.20 - $3.55
4" x 8"	$3.30 - $3.63
8" x 8"	$3.60 - $3.90
4" x 8" Disc	$3.45 - $4.10
8" x 8" Disc	$3.75 - $4.12
Stair Trim 8"	$1.90

Note: All sizes quoted above are for 3/8" tile thickness

The major competition to the Canadian made quarry tile comes from outside North America. Italy, West Germany, Spain, Brazil, Germany, Korea, Japan and England (ie. Wooliscroft and Ruabon with its Heather Brown line of tile) all produce quarry tile and sell it in Canada. As an example, Korean quarry tile sized at 4" x 8" x 3/8" sells for $2.65. The British version is approximately the same price as Canadian tile as a piece 8" x 8" x 3/8" sells for $3.75. Foreign companies rely on price to be competitive.

Noteworthy by its absence from the above list is the United States. Though the Americans do produce quarry tile, it is not found in the Canadian market because it is much more expensive. No prices could be quoted by Canadian distributors for comparative purposes. Higher labour costs, exchange rate fluctuations and trade agreements were all cited as problems affecting the pricing decision faced by American manufacturers. The Americans do offer a floor brick which does compete (along with carpeting) with quarry tile as an alternative floor covering.

Further foreign companies manufacture tiles that are only similar to quarry tile (ie. tiles that exhibit similar properties). The West German line is an extruded ceramic tile. The Italian line is mono-cotuitous (spelling unsure) and single-fired. The Japanese line is patterned and is similar to mosaic tile. Occassionally architects specifically request quarry tile for use in their building projects. This eliminates the competition and helps the Canadian company.

The Canadian company competes on two other fronts. First, for large orders that cannot be filled from stock, quarry tile must be shipped to Canada which can take from five to ten weeks to arrive. Clifton Ceramic maintains a three week lead time for production of any large order. Thus they compete by being fast and reliable. Second, they lobby the government both Federal and Ontario) to ask that any of their contracts for tile flooring request Canadian-made tile only. As they are the sole manufacturer of quarry tile in Canada, tile for the job must be purchased from one of their distributors.

Purchases are rarely made through the company directly but rather they use a series of tile distributors to facilitate sales. The largest distributor of quarry tile in Canada is Olympia Tile which has sales offices from coast to coast. Second to them is Central Tile Supply Company which does most of its business in Ontario, Quebec and British Columbia. The third largest distributor is RAMCA Tile located in Toronto serving the Ontario market while Ames Brothers, the next largest, serves the Prairie provinces only.

None of these four companies actually install the tile. They act as selling intermediaries only. Installation is accomplished through smaller tile contractors located in each major Canadian city. Installation costs are approximately equal to tile costs. Installing $10.00 of tile probably costs $10.00 for labour and other materials.

People who install shopping centre floors, floors in office complexes and large lobbies, and industrial floors use the following questions to determine what kind of floor tile to purchase:

1. What colours, patterns and/or textures of tiles are needed for the project ?
2. What are the technical qualities for the tile as outlined by the architect or engineer ?
3. If the project is for government, does the tile meet their specifications ?
4. Is the price within an appropriate range for the project to be undertaken ?

FOAM-TYPE INSULATION

Not being all that familiar with ceramics, it is unclear to this researcher as to what is "foamed ceramic material". However, if the descriptions found have been correctly interpreted, foamed ceramic material is quite light and easy to cut and shape. It is for this reason that design engineers suggested that it could be used in place of "styrofoam-type" insulation.

The insulation market can be broken down into five types of insulating materials: polyurethane foam, extruded polystyrene (Styrofoam), expanded polystyrene, fibreglass batts and other insulators (like rock wool, vermiculite). In 1984, the amount of insulation sold in Canada amount to $100 million and Ontario accounted for 50% of that total.

Polyurethane foam is injected into walls in a semi-liquid state and expands to fill empty wall cavities (much like shaving cream expands upon leaving the can). Polyurethane insulation companies are legion. There are few costs associated with setting up such an operation. Thus there are polyurethane insulation companies inc every small, medium and large city in Canada. These companies are also distinguished by the lack of one dominant player (ie. there is no chain of these companies which dominate the market).

Both expanded and extruded polystyrene come in sheets and are used for insulation in the construction of new homes or in retro-fit situations under aluminum/vinyl siding. Fibreglass batts are primarily used to insulate rooves and attics though some walls are filled with the batts. The A.R.C. material seems best suited to compete with the extruded and expanded polystyrene insulation sheets. Its impermeability and frost resistance seem to be ideal properties for insulation materials. The Russians have reported using foamed slag-ceramics for insulation in many successful tests.

Only one company in Canada manufactures extruded polystyrene insulation and that is Dow Chemical of Sarnia. Their product is protected under patent and their trade name (which has nearly become generic) is Styrofoam SM insulation. Commonly the material is available in 2' x 8' sheets with thicknesses varying from one to four inches. Styrofoam is white in colour but the sheets have a pale blue coating applied to them before they reach the market.

Styrofoam has a rating of R5 per inch of insulation. This compares to a fibreglass batt with a rating of R3.4 per inch of insulation. Styrofoam has other attractive properties besides its good insulating rating. These are: 1) it does not rot; 2) it incurs 0.7% water absorption; 3) it has high compressive strength of 30 pounds per square inch; 4) its permeability rating is 0.6/inch; and 5) it provides a type 2 vapour barrier.

These factors combine to make styrofoam ideal for use not only under aluminum or vinyl siding, but as insulation for basements and large halls wherever large, flat walls exist. Another advantage to styrofoam insulation is that it can be attached to these sufaces by strapping. Fibreglass batts are not easily attached in this way !

Dow views its largest market as the "Do-It-Yourselfer" upgrading the insulation in his or her home. Residential building starts have been low for the past few years and Dow sees slow growth (1 to 2% per annum) here in the future. Building starts in the commercial sector have also been low but Dow does expect medium growth (5 to 8% per annum) for this market in the future.

Dow's competition is restricted to expanded polystyrene insulation made in Canada. It is worth noting that no foam-type insulation is imported from the United States. Shipping costs are prohibitive. As one industry source stated, "It would be just like shipping truckloads of air from the United States to Canada !" In the United States market, Dow's largest competition comes from a company called Foamular.

Expanded Polystyrene is not as good an insulator as styrofoam. It has a rating of R3.64 per inch of insulation (but this is still better than fibreglass). It is also available in 2' x 8' sheets with thicknesses varying from one to four inches. Other sizes of both products are available because building supply companies need larger sheets for some odd-sized walls. A summary of sizes and prices can be found below.

Summary of Sizes and Prices

	Sizes	Prices (where available)
Styrofoam	2' x 8' x 1"	\$5.50 - \$6.50
	2' x 8' x 2"	\$11.00 - \$12.00
	2' x 4' and 4' x 8'	
Expanded Polystyrene	2' x 8' x 1 3/8"	\$3.45
	4' x 8' x 1"	\$4.99
	4' x 8' x 2"	\$9.99

As the summary indicates, expanded polystyrene competes on the basis of price. There are many producers of expanded polystyrene insulation; approximately 20 in Canada. Breaking this down further, there are five producers in Quebec, four in the Maritimes, one each in Manitoba and Saskatchewan, and two each in Alberta and British Columbia. In Ontario, there are five producers of expanded polystyrene insulation of which the three largest are: 1) REACH Products; 2) MORVAL Durafoam; and 3) PEACOT Plastics. Producers are localized serving regional markets.

REACH Products of Toronto report similar markets to Dow Chemicals. They sell 40% of their product to the residential insulation market and 30% to the commercial insulation market. Unlike Dowm the other 30% of their output goes to packaging insulation (an area they were unwilling to discuss).

Expanded and extruded polystyrene account for $40 million of insulation sales annually in Canada. Both products are sold extensively through building supply outlets like Beaver Lumber and Home Hardware. It is not unusual for an outlet to stock both types of insulation in large quantites and fill orders from their own warehouses. To order product from the manufacturer, these outlets are visited regularly by company salespeople. Dow often goes further by engaging in cooperative advertising with the building supply companies. These ads are directed either at home owners or building contractors.

Dow also sends salespeople to meet with engineers and architects in an attempt to sell them systems of bulding products. The insulation becomes part of a package which included siding, roofing and trim. Even if the system does not sell, attempts are made to get Styrofoam SM brand insulation listed in the design specifications for a building project.

People buying "foam-type" insulation use the following questions to determine what brand of insulation to purchase:

1. What "R" rating is necessary for the job ?
2. How much space is available for the insulation ?
3. What are the specifications cited by the engineer/architect ?
4. Is the price reasonable for the job to be done properly ?

SANITARYWARE

In Canada, there are basically three types of material used to produce sanitaryware: 1) Stainless Steel; 2) China; and 3) Enamelled Steel. Not surprisingly, companies that produce sanitaryware offer all three types of material to their customers. The four largest stainless steel sanitaryware manufacturers in Canada are: 1) American Standard; 2) Crane; 3) Waltec; and 4) Wessan. For sanitaryware made of china the four largest companies are: 1) Crane (Montreal); 2) American Standard (Toronto); 3) Waltec (Cornwall); and 4) Kohler.

The Abrasion-resistant ceramic material is probably best suited to produce sanitaryware that would compete directly with china. The Russians and the British both report successful uses of slag-ceramics in this way.

In 1984, the china sanitaryware market in Canada accounted for approximately $15 million of sales. The two largest companies, Crane and American Standard, each accounted for about 25% of that figure with Crane being slightly larger in sales volume. Both of these firms compete by offering a full line of standard sanitaryware fixtures. Kohler, instead, focusses on an "elite" line of designer sanitaryware fixtures.

The market is also subject to foreign competition from Mexico, Israel, Italy, Germany, Britain and Brazil, who compete on a lower price basis, and from the United States, who competes by offering coloured and designer bathroom fixtures. The American competition comes mainly from the United States counterparts of Crane and American Standard.

Four basic products make up the line of sanitaryware. These are: 1) the toilet; 2) the sink; 3) the bathtub; and 4) the urinal. For each of these items the standard colour offered is white but, for a premium price, six other colours are available (pastel shades of off-white, blue, yellow, brown, grey and green). Typical prices for these items are indicated below.

Summary of Product Line and Prices

Item	Price
Urinal -- wall hung -- white	$238
-- wall hung -- coloured	$476
-- floor model -- white	$308
-- floor model -- coloured	$616
Toilet -- white	$134
-- coloured	$172
Bathtub -- white	$213
-- coloured	$245
Sinks -- white	$51
-- coloured	$60

For the toilet, there are four basic designs: 1) the One-Piece Toilet, which operates on a gravity fed basis; 2) the Siphon Jet Toilet, commonly found in office buildings; 3) the Reverse Trap Without Jet Toilet, which is the most powerful toilet and is used in below ground level areas; and 4) the Blowout Bowl Toilet, which has the flush valves on top. Features can vary for each model but these differences are mainly cosmetic only.

Bathtubs also are available in four basic designs: 1) Sunken or Recessed bathtubs that fit into the floor; 2) Whirlpool or Jacuzzi type tubs; 3) Stand Alone bathtubs reminiscent of early 1900's tubs; and 4) Wall and Floor attached tubs common in most homes. Sinks come in three basic models: 1) Stand Alone sinks which use a pedestal for support; 2) sinks designed to fit into a vanity; and 3) Wall Hung sinks common in public restrooms.

All of the products listed above are sold to both the commercial and residential sectors. Urinals, however, are sold only to the commercial market. Urinals are available in just two models: 1) Wall Hung; and 2) Floor Models. Colour is not very important here and should a client wish units in a colour other than white, a special batch would need to be made.

Sanitaryware products are sold through plumbing wholesale outlets across Canada. Independent wholesale outlets are visited periodically by company salespeople to advise firms of new products, styles and prices. These outlets carry little if any stock, so all orders are filled directly from the plant. Crane and American Standard attempt to keep the time to fill an order down to three weeks.

The companies themselves also own some sales outlets in large cities. They operate like the independent stores but the salespeople have the added responsibility of bidding on contracts for bathroom fixtures for any new buildings. Also Crane and American Standard lobby architects and engineers to have their products listed as part of the specifications on a building project. The only drawback to this strategy is that frequently architects list both products as being equivalent in the specifications.

People buying sanitaryware use the following questions to determine what brand to purchase:

1. Is the style or appearance of the product appropriate for the job ?
2. Is the appropriate colour available ?
3. Can the proper quantity be delivered on time ?
4. Is the price of the product competitive ?

AIRPLANE AND MISSILE NOSE CONES

It should be noted that this section was the most difficult to research and most vague when it comes to details. There is even some uncertainty in the details given as companies were very reluctant to talk about the ventures in this area.

The leading edges of planes and missiles help to slice the wind and create the air currents needed to help these vehicles fly. These leading edges are therefore the most susceptible to wear through the abrasion of particles of dust, etc. suspended in the atmosphere. One of the edges referred to would be the nose cone and at present this part of the vehicle is made of very abrasion resistant metal or in some cases glass ceramics. The abrasion-resistant slag ceramic material developed in Canada, could have some applications in this work.

Though aircraft are assembled in Canada, it appears that no Canadian firm is involved in the manufacture of nose cones either for missiles or aircraft. Further, when aircraft companies were approached to find the names of companies producing the nose cone, they refused to release the information. A different tact was chosen. As some nose cones are made from glass ceramics, North America's leading manufacturer of glass ceramic material, Corning, was approached for details.

Understandably skeptical talking over the telephone to a Canadian about matters that they felt should be kept secret the following bits of information were gained. Unlike products considered to this point, nose cones are not pre-fabricated and stocked in a warehouse. Design engineers who get involved with the aircraft engineers act as the salesmen. They work with the designer in the early stages and suggest designs and shapes suitable for the application. These designs are then brought back to the plant where prototypes are made. Design specifications are exact and there is little tolerance for error or product failure. The prototype planes (or missiles) are tested and refined and the nose cones may undergo several changes before the aircraft design is approved. All along Corning's engineers are working with the aircraft company.

Once final approval is given to the overall design, orders are taken for the airplane. Because of the cost of missiles or airplanes, sales are measured in the hundreds not the millions. Again for safety reasons, nose cones are not massed produced but turned out with a great deal of care one at a time.

No dollar figures were released but the cost of a nose cone probably runs in the thousands of dollars and the engineering advice along the way might cost a firm several hundred thousand dollars. In other words, the research and development costs of the nose cone are more important than production costs. This would not be a high turnover product.

Colour and styling are not important and there is no such thing as standard sizes or prices. The individual nature of the nose cone does not allow much comparison to be made. The major markets for such a product would be Canada and the United States. In fact, where the Canadian government would be involved, a Canadian company that could participate in the production of a nose cone might be preferred to an American company.

Dollar or unit sales figures are not available and Corning would not release any dollar sales figures. Neither the British nor the Russians claim to have used slag ceramics in this manner though the Russians do make mention of the use of glass ceramics in American missiles.

It appears that airplane companies use the following questions to determine what company might participate in the nose cone design for a new airplane:

1) Does the company have the engineering expertise ?

2) Can it supply prototypes of the product ?

3) Is the firm reliable in its work ?

4) Have we (the airplane company) worked with them before ?

RECOMMENDATIONS

From an examination of the four possible uses for the abrasion-resistant material, it would appear that the most feasible would be the production of floor tile. Technology does exist that would allow the A.R.C. tile to be made in different colours and probably different patterns. It is also necessary that floor tile be wear-resistant. As the tile is made from slag, a cheap and abundant resource, the price should be more than competitive. The only drawback is the lack of fit between the market served by A.R.C. tile and Floor Tile.

Another market that seems to have some attractiveness is the "foam-type" insulation market. Though it is unsure what a foamed slag ceramic would be, its impermeability to water, high crushing strength and frost resistance are in its favour. The product here does not capitalize on abrasion-resistance but merely on the slag-ceramic material. Perhaps simpler processing could be undertaken to produce a more cost-efficient material for use here. There are two other uncertainties to consider: 1) What would be the "R" rating of a foamed slag-ceramic insulation material ? and 2) Can it be manufactured in a plant set up for tile production ?

The other two uses seem to be marginal at best. The nose cone for missiles and aircraft would not use a great deal of slag and would actually require much more man time than manufacturing time. There would be little fit between A.R.C. tiles and nose cone development. As for sanitaryware, the market is somewhat larger but there are three drawbacks: 1) Can A.R.C. sanitaryware be produced in the standard colour of white ? 2) Can a plant set up to manufacture tile also be equipped to handle sanitaryware molds ? and 3) Given the size of sanitaryware fixtures, would the production of these items require excessive storage space ?

There are also two footnotes to this work. First in performing this research some cost figures were uncovered for the production of slag-ceramic materials in Russia. The figures are 15 years old but might still give some insight into the cost problem. Secondly, it appears that the British have refined the procedure required to make the slag-ceramic material. They have eliminated much of the heating process and appear to be about to commercialize their process. This might change the situation faced in Canada by CANMET and ORF !!

REFERENCES

1. Conversations with Mr. W. Marchison, Clifton Ceramic Tile Inc., Kingston, Ontario.
2. Conversations with Mr. John Millan, Olympia Tile Company, Toronto, Ontario.
3. Conversations with Ms. Laurel Hastings, Central Supply Company, Toronto, Ontario.
4. Conversations with Mr. Andy Piotrowski, Dow Chemical of Canada Inc., Mississauga, Ontario.
5. Conversations with Mr. W. Franks, REACH Products Inc., Toronto, Ontario.
6. Conversations with Mr. P. Stinson, Crane Plumbing Supply Company, Hamilton, Ontario.
7. Conversations with Mr. Marcel Deschamps, Crane of Canada Ltd., Montreal, Quebec.
8. Conversations with Ms. Susan Allen, Corning Glass Works, Houghton Park, Corning, New York.
9. Glass Ceramics and Photo-Sitalls, Anatoli I. Berezhnoi, Plenum Press, New York, New York, 1970.
10. Marketing Study for Abrasion Resistant Ceramic Tiles, Phase I, 1984.

Glass or glass-ceramics may be used to manufacture the spherical buoys used for the experimental instrumental underwater platforms used by the United States Coast Guard and Geodetic Survey, which are anchored by chains at a depth of 30 m. These buoys have to withstand hydrostatic pressures of 190 kg/cm^2 for a period of six months. Model samples manufactured from glass-ceramics were tested at maximum compression stresses of the order of 25,000 kg/cm^2, which is considerably higher than what is required.

11. COST OF GLASS-CERAMICS

The economic advantages of glass-ceramics are determined by the low cost of the original nonstrategic raw materials and by the possibility of shaping glass articles from the glass melt by rapid conventional techniques. According to some data, glass-ceramics may cost from 30 cents per pound up, depending on the type, finishing, shape, and number of articles, as well as on other factors [705].

Tables 82-84 show the cost (ca. 1964) of piping, tubing, plates, and disks made of Pyroceram 9608, produced by Corning Glass Works [21].

According to Japanese data cited by Tamura [549], the cost of a production unit of a glass-ceramic of lithium aluminosilicate composition, for the production of which 1 kg of Li_2CO_3 was used, is approximately 1000 yen, whereas the cost of 1 kg of glass is 600 yen. The cost of glass-ceramics may be decreased if less expensive lithium materials, such as spodumene, petalite, and lepidolite, are used as raw materials. The cost of one ton of such raw material is approximately 50,000 yen, and the cost of 1 kg of the glass to be used for production of the glass-ceramic is less than 70 yen; it is thus cheaper than the cost of lead-containing electrovacuum glass.

The Soviet investigators Kitaigorodskii and Bondarev [46] performed preliminary calculations with respect to the technical and economical efficiency of structural materials made of glass-ceramics based on metallurgical slags; these calculations show that the production costs of a plant producing sheet glass-ceramic with a capacity of 5 million m^2 per year are estimated as 5,700,000 rubles, whereas the production costs of a plant producing ceramic tile and of the same capacity are 9,800,000 rubles. The cost of 1 m^2 of glass-ceramic facing tile is half that of ceramic floor tile, and a glass-ceramic kitchen sink is six times less expensive than an enamel-coated cast-iron kitchen sink [685]. Glass-ceramic piping is considerably less expensive than metallic piping. Em-

Table 82. Cost of Piping and Tubing Made of Pyroceram 9608

Outer diam., mm	Wall thick-ness, mm	Length, mm	Unit price, US dollars	Outer diam., mm	Wall thick-ness, mm	Length, mm	Unit price, US dollars
			Piping				
3.0	0.60	1219	0.35	19.1	0.76	3048	7.05
6.0	1.00	1219	0.70	19.1	1.52	3048	10.15
6.4	1.19	1219	0.90	19.1	1.00	1219	4.05
8.0	1.00	1219	1.00	25.0	1.50	1219	5.15
9.0	1.00	1219	1.18				
10.0	1.00	1219	1.30	24.5	2.38	1219	12.70
12.7	1.60	1219	2.55	30.0	1.8	1219	7.35
15.0	1.20	1219	2.40	31.0	3.0	1016	10.25
15.9	2.16	1219	4.65				
			Tubing				
3.0	—	1219	0.50	6.4	—	1219	1.50
6.0	—	1219	1.10	12.7	—	1219	5.90

Table 83. Cost of Round Disks Made of Pyroceram 9608

Diameter, mm	Unit price in US dollars at thickness, mm						
	6.4	9.5	12.7	15.9	19.1	25.4	28.6
25.4	0.45	0.50	0.65	0.90	1.00	1.10	1.80
50.8	0.60	0.95	1.05	1.65	1.75	2.00	3.25
76.2	1.00	1.45	1.75	2.50	2.75	3.25	4.75
101.6	1.50	2.10	2.65	3.60	4.00	4.75	7.00
127.0	2.00	2.80	3.50	5.00	5.40	6.25	9.50
152.4	2.60	3.60	4.60	6.50	7.00	8.25	13.20
203.4	4.10	5.75	7.25	10.00	11.00	13.00	20.00
254.0	5.80	8.00	10.00	14.50	16.00	18.50	28.00

Table 84. Cost of Square and Rectangular Plates Made of Pyroceram 9608*

Area, dm²	Unit price in US dollars at thickness, mm						
	6.4	9.5	12.7	15.9	19.1	25.4	28.6
0.26	0.20	0.25	0.30	0.35	0.45	0.55	0.75
0.58	0.45	0.50	0.65	0.80	1.00	1.15	1.70
1.03	0.75	0.90	1.10	1.40	1.70	2.10	3.05
1.61	1.20	1.40	1.75	2.20	2.65	3.25	4.75
2.32	1.70	2.00	2.50	3.15	3.85	4.70	6.80
3.16	2.30	2.75	3.50	4.30	5.20	6.40	9.25
4.13	3.00	3.60	4.45	5.65	6.80	8.30	12.10
5.23	3.80	4.55	5.60	7.15	8.60	10.55	15.30
6.45	4.70	5.60	6.95	8.80	10.65	13.00	18.90
7.74	5.65	6.70	8.30	10.60	12.75	15.60	22.70
11.61	8.50	10.60	12.45	15.80	19.10	23.40	34.00
15.48	11.30	13.40	16.60	21.00	25.50	31.20	45.40
23.23	17.00	20.00	25.00	31.60	33.30	48.80	68.00

* Maximum size of the plates is 254 × 914 mm.

ploying glass-ceramics in housing construction can result in considerable savings.

The processing of waste slages into glass-ceramics can represent a great benefit to the economy.

From Glass Ceramics and Photo-Sitalls by Anatolii I. Berezhnoi, Plenum Press, New York, 1970. Pages 410-412.

EROSION-RESISTANT GLASS-CERAMICS MADE BY DIRECT CONTROLLED COOLING FROM THE MELT

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Summary

The objective was to develop a pilot-plant facility to produce glass-ceramic ('Silceram') by a novel process. In this, a silicate melt is converted to a fine-grained pore-free ceramic during a controlled-cooling heat-treatment, removing the need for reheating which is essential to conventional glass-ceramic processing. The new heat-treatment programme offers a substantial saving in thermal energy. Glass-ceramic has been produced at the pilot-plant principally as flat tiles, but also by casting into special shapes. These products have been made from melts whose components were pure oxides and carbonates, and also from mixtures of blast-furnace slag and colliery shale with added nucleating agent. These industrial by-products not only reduce the raw material cost but improve the efficiency of melting and refining. The new material has superior mechanical properties. The crystal size of the major silicate phase is about 2μm and the porosity is close to zero. The high strength and hardness are associated with excellent resistance to erosion by fluid-borne particles. Estimates of manufacturing cost for flat product 'Silceram' on the 1000 tonne per year scale show it to be strongly competitive with other erosion-resistant materials used industrially. The cost benefit for more complex shapes is better still.

1. INTRODUCTION

Glass-ceramics constitute a class of materials which are shaped by conventional glass-forming techniques but, during a subsequent heat-treatment, are transformed to fine-grained ceramics of extremely low porosity. The microstructure of a glass-ceramic is associated with a number of desirable properties which are otherwise difficult to achieve, notably high mechanical strength, great hardness and resistance to abrasion and erosion. Like conventional ceramics, glass-ceramics are relatively chemically inert, with the added advantage over sintered ceramics of having extremely low porosity as a result of the fusion stage of the process. This combination of properties has encouraged interest in industrial applications as constructional materials, particularly where conditions of wear due to erosion may be severe. Examples of such conditions occur at power stations in the transportation of coal and ash, at mines in the transportation of coal, spoil and ores and at steelworks in the conveying of furnace burden and slags, and in coke ovens. Other applications include the provision of pipework to convey dusts and slurries which are both mechanically and chemically corrosive. Tests so far carried out show the new materials to be highly competitive with conventional materials on the basis of combined cost and performance.

The crystallisation of glasses has, in the past, been avoided by glass manufacturers, as sporadic nucleation and crystal growth leads to very poor mechanical properties. However, if the nucleation and growth stages can be promoted in a controlled way to produce a highly crystalline material the properties can far exceed those of the parent glass. By careful choice of the glass composition and the addition of nucleating agents this can be achieved. In conventional glass-ceramics the glass melt is cooled to a chosen temperature in order to produce the nuclei from which the major crystalline phase will later grow. The temperature is then raised to enable the growth of this phase, then slowly cooled to room temperature. During investigations of the effectiveness of different nucleating agents on the crystallisation of a particular range of glasses based on blast-furnace slag it was found that one particular combination, ferric oxide and chromium oxide, enabled nuclei to be formed at the temperature at which crystal growth occurs. This meant that the process could be simplified to a single-stage heat treatment during cooling from the melt rather than the conventional two-stage treatment. These observations provided the foundation for the development of the new ceramic material called 'Silceram'.

The adoption of this direct-cooling heat-treatment, using the programme described below, can result in energy savings of about 60% when compared with the conventional glass-ceramic processing cycle. This follows from the removal of the necessity to provide heat for holding at the lower temperature for nucleation and then raising the temperature again for the crystallisation step. If the new material were manufactured on a sufficiently large scale, then further energy savings can be made by using molten slag freshly produced from the blast-furnace. Because the preferred composition for 'Silceram' manufacture contains 60% slag, then the saving in energy requirement for melting from the use of hot slag can be about 50%. Since a major proportion of the manufacturing cost of glass-ceramics is fuel cost for melting and refining, these energy savings are of great importance.

2. THE PROCESS

The objectives in building the pilot-plant were to understand and overcome the problems in going from the laboratory scale to a small production scale, and to produce sufficient numbers of samples for industrial testing. The largest samples that had been made prior to this study had been about 1kg, melted in crucibles in a gas-fired furnace. The pilot-plant is capable of melting 100kg in a batch process using an oil-fired, tilting furnace, shown in Figure 1. The melt has to be in a shallow pool because of poor transmission of infra-red radiation through the liquid and the hearth refractory must be capable of withstanding corrosion by the melt. Tests on various refractories showed that a magnesia-chrome satisfactorily withstood the action of the melt. The remainder of the furnace is constructed from a high alumina refractory with outer layers of insulating bricks and fibre blanket. The melt is held at a temperature of 1450 to 1500°C for three hours then cast into steel or sand moulds to produce flat or textured tiles and a variety of detailed shapes. The castings are then heat-treated for three hours in electrically fired kilns at a temperature of about 900°C, and allowed to cool slowly. The two kilns have a combined volume of approximately 0.8m^3 and can hold 75kg of cast product. During experimental runs the batch size was usually limited to 50kg to reduce wastage and shorten the procedure.

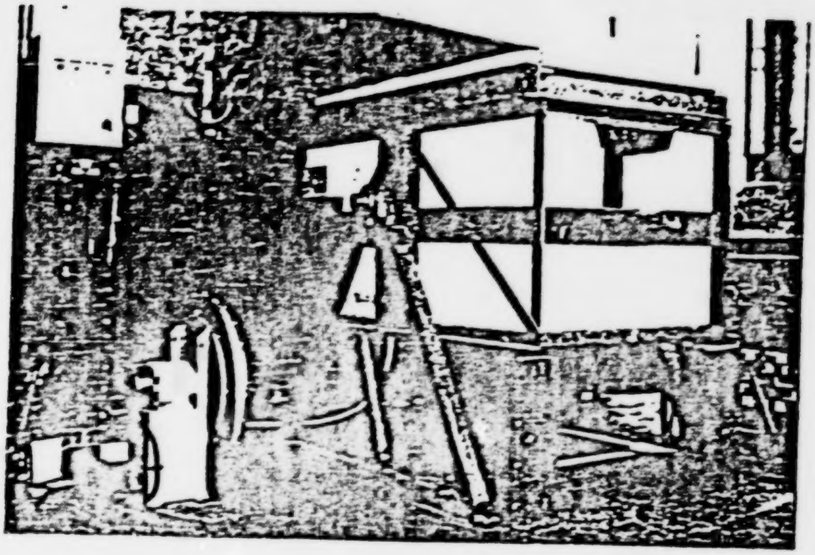

Figure 1. Melting Furnace

The composition limits of the 'Silceram' patent are shown in Figure 2, and all the successful samples produced to date lie within this range. A smaller range of preferred compositions is also shown. (1)

A number of raw materials can be incorporated into 'Silceram' batches including blast-furnace slag, pulverised-fuel ash, coal slag and colliery shale. The most successful materials have been made from a blend of sixty five parts blast-furnace slag to thirty five parts colliery shale, with an extra seven parts of nucleating agents and small amounts of pure oxides to correct small deficiencies in the base composition; this composition, SCR25, and the analysis of the finished product, with those of two other typical batches, are shown in Table I.

One hundred and fifty batches of twenty eight different experimental compositions have been melted and cast and the melting and casting conditions have been optimised for small-scale production. A wide range of sample sizes and shapes have been produced and a number of companies are performing larger scale testing than has previously been possible. The results of these tests will be reported in a later paper when they are available.

3. PROPERTIES AND TESTING

A wide range of physical and chemical properties have been determined for 'Silceram'. Although a large number of different compositions have been produced there is a remarkable similarity between their properties. Differences do occur when there are very large differences in microstructure, for example large crystals which tend to produce microscopic shrinkage voids or large amounts of residual glass. Even when there are considerable differences in microstructure this does not mean that there will be any significant differences in properties. For example, Figure 3 and 4 show the microstructures of three different materials, a pure oxide material made on the laboratory scale, SCF5, a pure oxide material made at the pilot-plant, SCR19, and a slag/shale batch also made at the pilot-plant, SCR25.

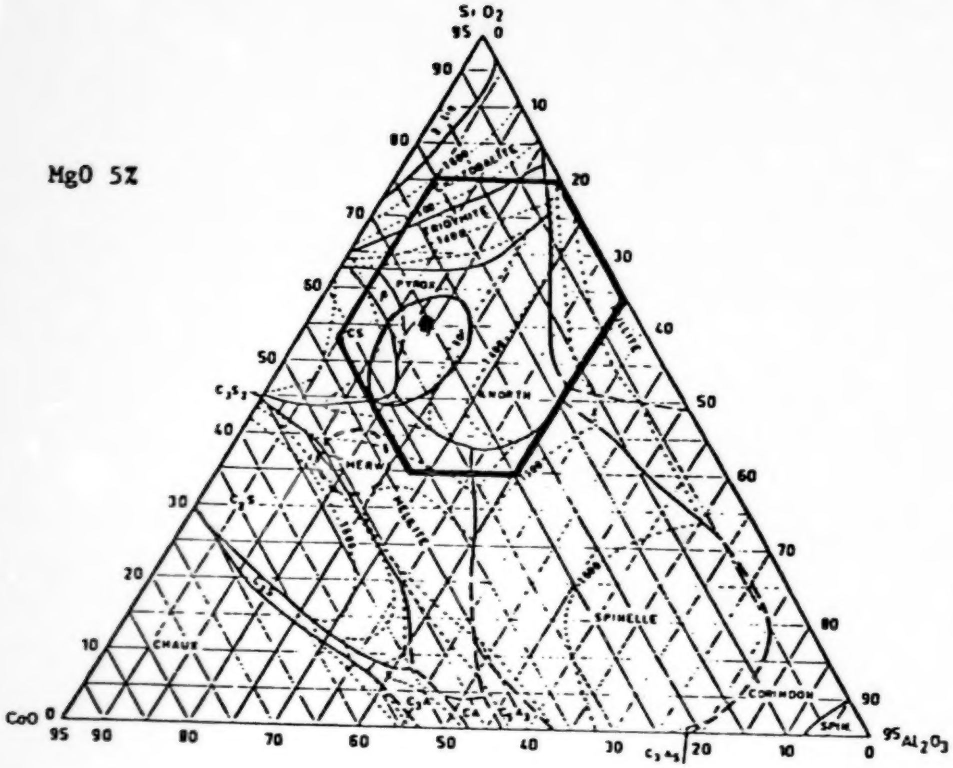
MgO 5%
SiO2
95
0
90
10
80
20
70
30
60
40
50
50
40
60
30
70
20
80
10
90
CaO 0
95
90
80
70
60
50
40
30
20
10
0
95 Al2O3
TRIDYMITE
1600
PYROX
CS
ANORTH
C3S2
MERW
C2S
MELILITE
SPINELLE
CHAUX
C3S
C3A
CA
CA2
C3A5
CORINDON
SPIN

Figure 2. Phase diagram for $CaO-Al_2O_3-SiO_2$ system containing 5% MgO (after reference 2)

- - - - typical blast-furnace slag compositions

● composition SCR25

—— preferred compositions

━━ 'Silceram' patent range (reference 1)

The sample of SCF5 shows a highly dendritic structure with crystal extensions of up to 30μm, and quite a large amount of residual glass. The microstructure of SCR25 shows some similarities in that there is a degree of dendritic structure, but much more compact. The third sample, SCR19, has some areas of extremely fine structure with inclusions of much coarser crystals, surrounding spinel crystals of about 2μm in size. These areas of coarser crystallisation are always associated with large spinel crystals, but the reverse is not always true.

The properties of these three materials, shown in Tables II and III, are remarkably similar and it is likely that the other properties shown in Table IV will be equally close. The fact that the much finer structure exhibited by SCR19 does not seem to affect the properties may be due to the presence of the clusters of much coarser crystals. If these can be removed

TABLE I

Compositions of selected 'Silceram' samples

Material	Component	Composition of batch (parts by weight)	Analysis of product (parts by weight)
SCF5	CaO	20	16
	MgO	14	10
	Al_2O_3	10	15
	SiO_2	56	59
	Fe_2O_3	3	3
	Cr_2O_3	1.3*	0.6
SCR19	CaO	27	23
	MgO	7	6
	Al_2O_3	15	14
	SiO_2	51	57
	Fe_2O_3	4	5
	Cr_2O_3	1.5*	0.9
SCR25	Slag	65	-
	Shale	35	-
	CaO	-	27
	MgO	1**	6
	Al_2O_3	0.5**	14
	SiO_2	-	53
	Fe_2O_3	4**	4.5
	Cr_2O_3	1.5*	1.1

* added as $Na_2Cr_2O_7$

** supplement to component in slag/shale

TABLE II

Modulus of Rupture

Material	Modulus of Rupture (MPa)	Specimen dimensions (mm)	Span (mm)
SCF5	180 ± 15	2 x 4 x 25	20
SCR19.5	138 ± 8	4 x 4 x 35	25
SCR25.1	149 ± 6	4 x 4 x 35	25
SCR19.5	100 to 110	10 x 30 x 120	100

then it is hoped that the properties can be further imporoved beyond those of the laboratory material, SCF5, which has been used as standard for comparison.

The results for SCF5 are for laboratory-made material and are included here for comparison with material produced at the pilot-plant. The small specimens were cut by diamond wheel from the cast tiles and the face of each to be in tension was polished, whereas the large ones were as cast. Modulus of rupture has been calculated from the breaking load in three point bending. As can be seen, the large bars of SCR19 gave a lower result than the smaller ones from the same material. However this is to be expected, since the strength properties of ceramics and glass-ceramics are determined by the presence, size and abundance of flaws in their structure and at the surface, so that the lower value is still a good result from a very much larger thickness of material subjected to stress.

TABLE III

Erosion Resistance

Material	Weight loss under test conditions (mg)	Test conditions used
SCF5	11.7 ± 0.5	(a) Erodant : sand, 100-150μm, 830g Impact angle : 90° Sand flow rate : 120g/min^{-1} Velocity at target : 15 ms^{-1}
SCR19.5	12.3 ± 1.4	
SCR25.1	12.5 ± 1.7	
SCR25.1	24.4 ± 4	(b) Impact Angle : 45° Sand flow rate : 190 g/min^{-1} Velocity : 25 ms^{-1} Other conditions as (a)
Cast Basalt	38.1 ± 1	
SCR25.1	20.1	(c) Erodant : sand, 100-500μm, 830g Velocity : 13 ms^{-1} Other conditions as (b)
Cast Basalt	33.2	

These results show that the two new materials produced in large scale at the pilot-plant, SCR19.5 and SCR25.1, are almost as resistant to erosion as the laboratory standard, SCF5, and compare very favourably with 'cast basalt' which exhibits a mass loss 55 to 65% greater. When expressed as a volume loss the value for 'cast basalt' is still over 50% greater.

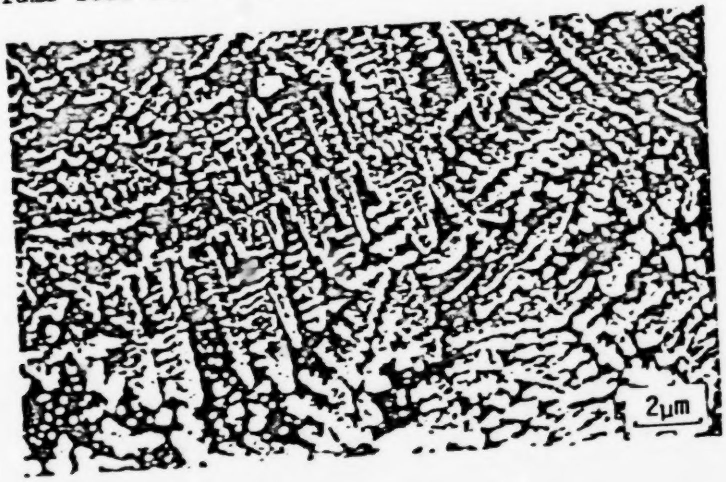

Figure 3.

Scanning electron micrograph of laboratory material 'Silceram' SCF5.

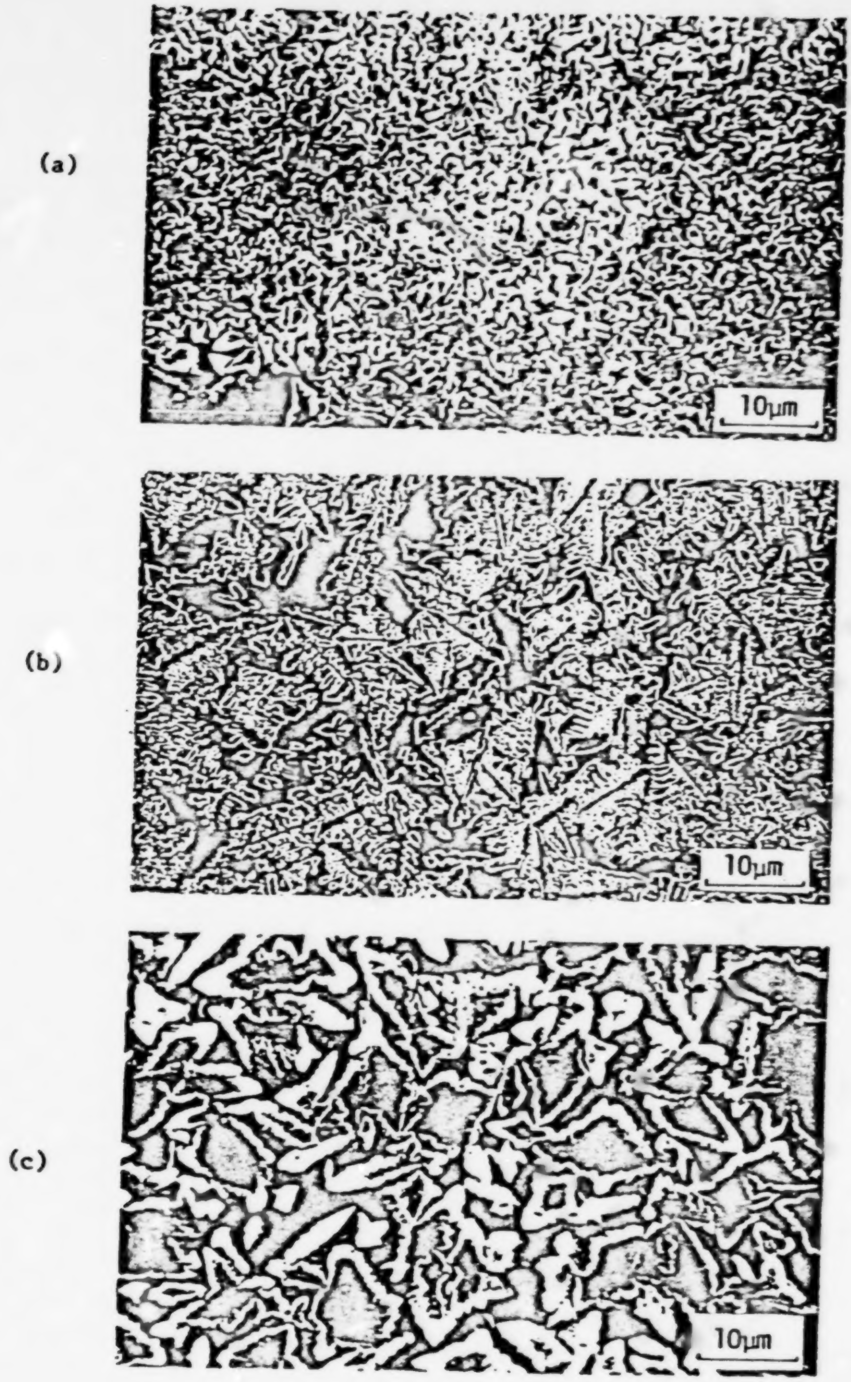
(a)
10µm
(b)
10µm
(c)
10µm

Figure 4. Scanning electron micrographs of pilot-plant material (a) SCR19-1; (b) SCR19-5; (c) SCR25-1.

TABLE IV

Properties of 'Silceram' SCF5

Density	2.9 gcm^{-3}
Fracture toughness	2.1 $MNm^{-3/2}$
Young's modulus	95 x 10^3 MPa
Compressive strength	850 MPa
Hardness (Vickers)	7.0 x 10^3 MPa
Coeff. of thermal expansion	7.5 x 10^{-6} K^{-1}
Thermal conductivity	1.76 Wm^{-1} K^{-1}
Viscosity of melt at 1450°C	6.0 Pas

4. MANUFACTURING COSTS

In making an assessment of the potential of the material, it has been assumed that in the first instance 'Silceram' will be exploited for its resistance to erosive wear by fluid-borne solid particles. The figures given here are estimates for the manufacture of flat tiles and sheet produced by a process similar to that operated at the pilot-plant, but on a larger scale, with consequent increase in size of melting furnace to a capacity of one tonne, and a larger number of heat treatment kilns. The costing exercise has been carried out on an assumption of 1000 tonnes per year of finished product. This quantity is equivalent to about 40,000 square metres of flat sheet, 1 cm thick and represents about a fifth of the U.K. market for erosion-resistant ceramics, determined on a tonnage basis.

TABLE V

Capital costs for 1000 tonnes per year production capacity

	£
Tank furnace, gas fired	24,000
Ancillary equipment, controls, etc.	5,000
Casting equipment for tiles and sheet	4,000
Heat-treatment kilns	22,000
Foundry equipment, mixers, etc.	10,000
Installation costs	5,000
	£70,000

The capital costs of plant for full-scale production, shown in Table V for 1000 tonnes per year capacity, are of course strongly dependent on the assumptions made concerning the nature of the products and the volume of production.

TABLE VI

Recurrent costs for manufacture of 1000 tonnes per year

	£
Staff costs, manufacturing, 6 persons	72,000
Staff costs, marketing, 2 persons	24,000
Services, at 25% of staff costs	24,000
Rent, 500 square metres	21,000
Gas	86,000
Electricity	12,000
Raw materials, including transport	10,000
Maintenance, at 10% of Capital Cost	7,000
Depreciation, at 15% of Capital Cost	10,500
	£266,500

The manufacturing cost per tonne of £266.50 shown in Table VI compares well with the cost of competitive materials such as cast basalt, even with the assumptions made in this analysis. Savings in fuel cost not included are those which would result from the use of recuperators in the burner supply (up to 50%). The attractiveness of the 'Silceram' is further improved by its better resistance to erosion than other ceramics of comparable cost. The advantage when both cost and performance are considered is very clear.

In order to make a complete assessment, attention must also be paid to the market for special shapes, to be used, for example, as nozzles, venturis and pipe-bends. These would be made by casting into sand moulds or shell moulds, techniques for which 'Silceram' is particularly suited. The selling price for such items is an order of magnitude higher, and the profit margin thus substantially larger.

Another potential application is in the manufacture of pipes for carrying liquids and slurries (e.g. drain pipes). Here the level of production would be as high as 100,000 tonnes per year, using continuous centrifugal casting. Some laboratory trials have been started with this application in mind.

5. CONCLUSIONS

The pilot-plant which was designed and commissioned during this project has been used to optimise melting, casting and heat-treatment conditions for the small-scale manufacture of 'Silceram'. This industrial ceramic is made by a novel process by direct-cooling from the molten condition, and is particularly suited for applications as an erosion-resistant material.

Laboratory work has shown 'Silceram' to have excellent mechanical properties and a high resistance to erosion by fluid-borne solids when compared with other ceramics in common use. Comparative tests of this kind depend upon the prevailing conditions, such as particle velocity, size and number density and angle of impact; tests under industrial conditions have shown the new material to be eroded 1.5 to 3.5 times more slowly than cast basalt, the material imported from outside the EEC area which currently dominates the market. Since the cost per tonne is close to that of cast basalt, the advantage on a cost-plus-performance basis is quite clear.

The techniques for forming 'Silceram' used in the work detailed here have, for the most part, been simple casting processes using steel and sand moulds. The silicate melt used is suitable also for shaping by spin-casting and shell moulding. There is thus scope for extending the process beyond the manufacture of flat products to more sophisticated techniques: on the high cost/low tonnage side, material may be cast as special shapes such as valve seats, nozzles and elbows; on the high tonnage side, 'Silceram' may be continuously spin-cast as pipes and tubes on a scale two or more orders of magnitude greater than the tonnage assumed in the economic analysis summarized in Table VI.

If the pilot-plant development is to be translated into an industrial process, a number of questions must be answered. If production is to be on a large scale using a continuous glass-melting tank furnace, then further information on melt behaviour and refractory performance would be required. If hot slag is to be incorporated as a raw material, then the use of cyclone mixers or rotary furnaces must be considered. It is intended that the problems of large-scale melting, as well as the techniques of spin-casting and shell moulding will be examined in the continuation of this work, in parallel with industrial exploitation.

6. REFERENCES

(1). Rogers, P.S. and Williamson, J. : Brit. Pat. 1 462 035
U.S. Pat. 3 799 836

(2). Cavalier, G. and Sandrea-Deudon, M. (1960) : Révue de Metallurgie, 57, 1143 - 1157.

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